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A contribution for the preservation of cellulose esters black and white negatives

Dissertação para obtenção do Grau de Doutor em Ciências da Conservação do Património, Especialidade em Ciências da Conservação

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Novembro, 2018

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Dedicated to my family

Acknowlegments

This research was developed at the Department of Conservation and Restoration, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa (FCT-UNL); *Arquivo Histórico Ultramarino* (AHU), *Sistema de Inventário do Património Arquitectónico* (SIPA); *Arquivo de Documentação Fotográfica* (ADF); *and Arquivo Fotográfico da Biblioteca de Arte da Fundação Calouste Gulbenkian* (BA-FCG)

The work was financially supported by Fundação para a Ciência e Tecnologia – Ministério da Educação e Ciência (FCT/MEC) with a doctoral grant (SFRH/BD/72560/2010).

First of all, I would like to thank my surpervisor, Professor Ana Maria Ramos, for her enthusiastic support, encouragement and guidance. To my co-supervisors Professor Dr. Bertrand Lavédrine and Professor Dr. António Parola, for guidance, important inputs and unconditional support.

To my thesis advisory committee (Comissão de Acompanhamento da Tese), Prof. João Lopes and Prof. Rudolf Gschwind, thank you both for the discussion and inputs on the PhD Thesis Plan Evaluation.

I would also like to thank all those responsible for the archives who have allowed me to access and study the collections selected for this work. I extend my most sincere thanks to Dr. Ana Martins, Dr. Alexandra Encarnação, Dr. Ana Paula Gordo and Dr. João Vieira, the vote of confidence and the support during the accomplishment of this work.

I am also grateful to all the people that contributed to this study and helped me during the experimental work and data analysis: Prof. Maria João Melo (DCR, FCTUNL) for the FTIR analysis and discussion; Prof. Joana Lia Ferreira for FTIR discussion, Prof. Márcia Vilarigues and Prof. Inês Coutinho (DCR, FCTUNL), for the EDXRF analysis; dear colleagues Eva Marisole Angelin and Artur Neves for the Raman analysis, Prof. António Candeias and Dr. Gabriela Carvalho (DGPC), for the artificial ageing chamber; Daniela Gomes (CENIMAT/I3N), for the SEM-EDS analysis; Dr. José Carlos Rodrigues (IICT) for the NIR spectroscopy.

To my fellow curators, photographers and archivists, Ana Coelho, Catarina Mateus, Catarina Gonçalves, Élia Marques, Lúcia Moutinho, Sónia Casquiço, Luisa Oliveira, Luís Pavão, José Paulo Ruas, Sofia Torrado, João Paulo Machado and Cátia Martins, thank you all for the encouragement and debate.

To all my fellow labmates, a special thanks for your friendship, for the exchange of ideas, and for all the fun times we shared. My most sincere thanks to Ângela Ferraz, Ana Margarida Silva, Filipa Pereira, Joana Silva, Marta Félix, Sara Babo, Sílvia Sequeira, Susana Belchior, Susana Sá and Tatiana Vitorino. To Ana Maria, for her patience and support.

To my friends, Catarina, Carolina, Luísa, Maria João, Ana, Rosa, Vanda, Isa and Pedro, thank you for always being there for me.

To my parents and brother, Diana and Daniel, I express a very special and warm thanks for all the support and patience during this long journey.

Part of the content of this Ph.D. dissertation has already been communicated in international conferences:

Oral communications

E. Roldão, A. J. Parola, João A. Lopes, A.M. Ramos, B. Lavédrine. Is it obvious? Not when we are dealing with cellulose nitrate. *Plastics Associated with Photographic Material,* Collaborative Workshop in Photograph Conservation, Foundation of the American Institute for Conservation *and* Center for Creative Photography, Tucson, Arizona, Estados Unidos da América, 14-18 de Março de 2016.

E. Roldão, A. J. Parola, João A. Lopes, A.M. Ramos, B. Lavédrine. How far can we see? The importance of accurate film identification. SOIMA 2015 – Unlocking Sound and Image Heritage, Bruxelas, Bélgica, 3-4 Setembro.

E. Roldão, A.M. Ramos. Polímeros semi-sintéticos em fotografia - o nitrato e o acetato de celulose. Encontro DigiFup – Digitalização e Tratamento da Filmoteca Ultramarina Portuguesa, Lisboa, 15 de Dezembro de 2014.

J. Silva, E. Roldão, A. J. Parola, A.M. Ramos, B. Lavédrine. Conservation of cellulose acetate photographic negatives: searching for new approaches. Conference CoMa 2013 – Safeguarding Image Collections, Royal Institute for Cultural Heritage (KIK-IRPA), Bruxelas, Bélgica, 31 de Outubro de 2014.

Poster

J. Silva, E. Roldão, A. J. Parola, A.M. Ramos, B. Lavédrine. New Approaches to Conservation and Preservation of Cellulose Acetate Photographic Negatives. InArt'13 - 1st International Conference on Innovation in Art Research and Technology, Évora, Portugal, 10-13 Julho de 2013.

Publications

Artur Neves, Eva Mariasole Angelin, Élia Roldão, Maria João Melo. 2018. New insights into the degradation mechanism of cellulose nitrate in cinematographic films by Raman microscopy. *Journal of Raman Spectroscopy*. DOI 10.1002/jrs.5464

Silva, J., Roldão, E., Parola, A.J., Ramos, A.M., Lavédrine, B.. Conservation of cellulose acetate photographic negatives: searching for new approaches. In: H. Arijs, eds. *CoMa 2013 Safeguarding Image Collection*. New Castle: Cambridge Scholars Publishing, pp. 149-162. ISBN -13: 978-1-4438-6818-1.

Abstract

Cellulose esters film-based negatives are known for their autocatalytic and irreversible decay. Over time, the ephemeral nature of these negatives became one of the most challenging issues for manufacturers, photographers, scientists, conservators, and overall caretakers that strive to foresee the decay of those composite materials and to develop preservation solutions.

The aim of this study is to introduce an analytical methodology that can inform the conservator not only about the nature of the film base but also about its condition in a non-invasive way. For this purpose, three hundred and sixty-one cellulose nitrate and cellulose acetate film-based negatives (1930s-1950s) from Portuguese institutions were selected. The selection of the cases studies relied on three main criteria: historical framework of the collection, film characteristics (type of support, format, producers/brands) and preservation condition. The selected negatives are representative of European and North American producers. The objects were studied using infrared and Raman microspectroscopies (μ-FTIR and μ-Raman), pH and hardness measurements, and Near infrared spectroscopy.

μ-FTIR analysis allowed to identify three types of film supports: cellulose nitrate, cellulose acetate and cellulose acetate butyrate. Based on the μ-FTIR analysis a correlation between molecular identification of the film base and notch codes was accomplished. For the set of negatives with cellulose acetate butyrate support no significant molecular changes were obtained, indicating that this type of negatives is considerably stable. Concerning cellulose nitrate and acetate-based negatives, μ-FTIR allowed to assess very different preservation conditions, ranging from Very Good to Severely degraded. A careful observation of the results obtained for cellulose nitrate-based negatives allowed concluding that negatives with spectral changes associated with severe degradation may have different degradation pathways according to thickness. Concerning cellulose acetate-based negatives, similar results were obtained. Moreover, the FTIR results enabled to identify a degradation trend associated with a film typology characterized by 'U' notch code and blue and brown anti-halation dyes.

Different plasticizers, namely camphor, phosphates and phthalates, were also identified by μ-FTIR and μ-Raman analysis.

pH and hardness measurements supported the spectral results obtained. It was confirmed that the de-esterification and chain-scission may be detected by their decrease. To confirm the chemical behaviour of cellulose nitrate-based negatives, an artificial ageing experiment (80^0C, 90% RH) was carried out, followed by the same analytical methodology. The results obtained for samples artificially aged support the findings obtained from the study of historical films.

These findings contribute for a review of the preservation strategies currently used, establishing a novel and non-invasive methodology which could provide accurate tools

for the identification of early degradation stages of negatives with cellulose nitrate and cellulose acetate supports.

By examining by μ-EDXRF and SEM-EDS the image layer of a set of cellulose nitrate negatives presenting colours, it was possible to identify the chemical elements present and correlate them with possible intensification and reduction treatments used to improve image density and contribute for the knowledge of Portuguese photographers working methods.

Keywords: cellulose esters, photographic negatives; condition assessment; hardness, preservation.

Resumo

Os negativos preto e branco com suporte em ésteres de celulose estão inerentemente associados à degradação autocatalítica que promove a perda irreversível das suas propriedades químicas e físicas. Ao longo do tempo, a natureza efêmera destes objetos tornou-se um desafio para fabricantes, fotógrafos, cientistas, conservadores e responsáveis por coleções, que se esforçam por prever a sua degradação e desenvolver soluções de preservação. Contudo, tendo em consideração a composição e a estratigrafia destes materiais, estas metas são difíceis de alcançar.

O objetivo deste estudo é o desenvolvimento de uma metodologia analítica não-invasiva que permita informar o conservador não apenas sobre a natureza da base do filme, mas também sobre o estado de conservação dos negativos. Para este efeito, foram selecionados trezentos e sessenta e um negativos com suportes em nitrato e acetato de celulose (das décadas de 1930 a 1950), que se encontram em coleções de instituições portuguesas. A seleção dos casos de estudo baseou-se em três critérios: relevância histórica da coleção, tipologias de filme (tipo de suporte, formato, produtores/marcas) e estado de conservação. Devido à ausência de indústria de produção de materiais fotográficos em Portugal, considera-se que os casos de estudo selecionados são representativos de produtores europeus e americanos. As espécies fotográficas foram estudadas através de microespetroscopias de infravermelho e Raman (μ-FTIR e μ-Raman), medições de pH e dureza e espectroscopia de infravermelho próximo (NIR).

A análise por μ-FTIR permitiu identificar três tipos de suporte: nitrato de celulose, acetato de celulose e acetato butirato de celulose. Os resultados obtidos permitiram estabelecer uma correlação entre tipos de suportes e *notch codes*. Relativamente ao conjunto de negativos com suporte de acetato butirato de celulose, não foram verificadas alterações moleculares significativas, indicando que este tipo de negativos é consideravelmente estável. No que diz respeito aos negativos com suporte em nitrato e acetato de celulose, a análise por μ-FTIR permitiu identificar negativos com estados de conservação muito diferentes, variando de Muito Bom a Muito Degradado. Os resultados obtidos permitiram concluir que existe uma forte relação entre os percursos de degradação e a espessura dos filmes, indicando que filmes com maior espessura tendem a sofrer de forte degradação e perda total de propriedades químicas e físicas. Relativamente aos negativos com suporte em acetato de celulose, os resultados obtidos por μ-FTIR permitiram identificar uma tipologia de filmes, com *notch codes* na forma de "U" e corantes anti-halo de cor azul e castanho, que consistentemente apresentam forte degradação. Estes resultados contribuem para uma revisão das estratégias de preservação de coleções ao indicar conjuntos de negativos que devem ser considerados prioritários devido ao risco elevado de degradação e contaminação da coleção.

As medições de pH e dureza suportaram os resultados espectrais obtidos, tendo sido confirmado que os valores de pH e dureza decrescem de acordo com a extensão da degradação (desesterificação e cisão de cadeia). Com o objetivo de confirmar os resultados obtidos para o conjunto de negativos com suporte em nitrato de celulose, foi efetuado um ensaio de envelhecimento artificial (80^0C, 90% HR). Seguindo uma

abordagem experimental idêntica para a análise das amostras envelhecidas artificialmente, os resultados obtidos suportam as conclusões apresentadas para o conjunto de filmes históricos.

Através de análise por μ-FTIR e μ-Raman foram também identificados diferentes plastificantes, nomeadamente cânfora, fosfatos e ftalatos.

Examinando por μ-EDXRF e SEM-EDS a camada de imagem de um conjunto de negativos foi possível identificar os elementos químicos presentes e correlacioná-los com possíveis tratamentos de intensificação e redução utilizados para melhorar a densidade da imagem.

Os resultados obtidos no decorrer deste trabalho contribuem para uma revisão das estratégias de preservação utilizadas atualmente, estabelecendo uma nova metodologia não-invasiva e fornecendo novas ferramentas que permitem identificar e avaliar o estado de conservação de negativos com suporte em ésteres de celulose. Acresce ainda o importante contributo deste estudo para o conhecimento dos materiais fotográficos presente nas colecções nacionais e também o trabalho de fotógrafos Portugueses.

Palavras-chave: ésteres de celulose, negativos fotográficos; avaliação do estado de conservação; dureza, preservação.

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Symbols and Notations

δ	Bending vibration
ρ	Density
μ	Micro
μ	Peak centre
ν	Stretching vibration
γ	Twisting vibration
M	Mass
V	Volume
ρ	Sandard error
ADF	Arquivo de Documentação Fotográfica
AHU	Arquivo Histórico Ultramarino
as	antisymmetric vibration
ATR	Attenuated Total Reflectance
BA-FCG	Biblioteca de Arte da Fundação Calouste Gulbenkian
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
CDA	Cellulose diacetate
CTA	Cellulose triacetate
CN	Cellulose nitrate
cm	centimetre
DGEMN	Direção Geral de Edíficios e Monumentos Nacionais
DGPC	Direção Geral do Património Cultural
DPP	Diphenyl phosphate
DS	Degree of substitution
DP	Degree of polymerization
ECC	Elmano Cunha e Costa
FCG	Fundação Calouste Gulbenkian
FTIR	Fourier Transform Infrared spectroscopy
HHI	Heritage Health Index
HS - GC	Headspace gas chromatography
HS-SPME-GC/MS	Phase microextraction-gas chromatography coupled with mass spectrometry
IR	Infrared spectroscopy
IHRU	Instituto da Habitação e da Reabilitação Urbana
m	medium
mm	millimetre
MN	Mário Novais
NIR	Near-infrared spectroscopy
NMR	nuclear magnetic resonance
OEA	Organic elemental analysis
s	Symmetric vibration
S	Strong
SEM-EDS	Scanning Electron Microscopy– Energy Dispersive Spectroscopy
SIPA	Sistema de Informação para o Património Arquitectónico
sh	shoulder

SP	San Payo
SN	Silva Nogueira
SG	Specific gravity
SEC	Size exclusion chromatography
SPME-GC	Solid Phase Micro Extraction gas chromatography
T	Temperature
t	time
TCP	Tricresyl phosphate
TPP	Triphenyl phosphate
TRFTIR	Total Reflectance Fourier Transform Infrared spectroscopy
vs	Very strong
vw	Very weak
VOC	Volatile organic compound
w	Weak
WWI	World War I
WWII	World War II

Chapter 1 - General Introduction

Chapter 1 - General Introduction

The history of photography is brief, yet its impact on mankind is immeasurable.(Norris and Gutierrez 2017, 18)

Since its invention in the beginning of the 19th century, photography became a means of communication and artistic expression, selected as *media* to record and document a wide variety of subjects, which are currently documents of our personal and collective memory, and part of our cultural heritage. Despite the vast technical, historical and philosophical discussions, photography is generically seen as […] a *science and an art […]* (Newhall 1982, i).

The broad acceptance and use of cellulose esters film-based negatives are one of the most expressive examples of the importance achieved by photography. From the end of the 19th century until now, the onset of film-based negatives has greatly contributed to the increasing use of photography. Therefore, plastic negatives may be considered the documenting media of society since the 20th century. Accordingly, it is possible to say that besides the intangible nature of photography there is also an inherent value associated with its materials, as it is a testimony of the technical and scientific achievements accomplished in the last two centuries.

To ensure the permanence of such valuable heritage, Portuguese cellulose ester film-based collections are studied in the framework of this research to develop insightful knowledge on the chemical and physical stability of these 'recent' materials as well as to establish innovative preservation actions.

Sustainability issues in the preservation of black and white cellulose esters film-based negatives collections

However, and this is important, keep the originals!!
José Orraca 2010, 33

Photography is still a medium through which scientific, technological, anthropological and social achievements are recorded, awarding it an unequivocal documental character. From the different type of photographic materials used since the late 19th century, cellulose esters film-based negatives are one of the most expressive examples of the scientific and technological achievements. The expressive impact of film-based negatives on society is nowadays reflected on the presence of huge quantities of plastic negatives in the collections of institutions from all over the world, demonstrating its wide acceptance and use (Pavão 1997, 13;Reilly 2010a, 569). According to a large survey carried out by the Heritage Health Index (HHI) in 2010, in some institutions in the United States, it was concluded that there are 57 million film-based negatives previous to the 1950s in that country (Norris 2011).

Donated, acquired, or as result of the institution's practice, photographs usually come in huge quantities (ranging from hundreds of thousands to millions of specimens). Despite the 'quantity of photographic objects', these sometimes are […] *invisible even to those who work with it every day* […] (Reilly 2010a, 567).

The invisibility of photographs is particularly noticed when it comes to photographic negatives. As James M. Reilly[1] described, negatives […] *are virtually unknown to the staff and unusual for research* […] (Reilly 2010a, 567). In part, negatives are relegated to obscurity due to the difficulty in accessing the image contents. This obscurity may also lead to unveiled treasures that we are not aware of. However, it may also be a 'poisoned surprise' if considering the chemical characteristics and the physical decay of cellulose esters film-based negatives (see Chapter 1).

Cellulose esters film-based negatives are known for their autocatalytic and irreversible chemical and physical decay (Valverde 2005; Lavédrine 2000b). In part, cellulose esters permanency or instability is also correlated with the fact of being the *oldest* plastics. Moreover, the experimental period associated with the invention and commercial production of cellulose ester film-based negatives is also indicated as a cause for the chemical and physical instability of those materials. In sum, the high flammability of cellulose nitrate, the lack of dimensional stability of the first cellulose acetate film-based negatives, or the chemical instability of both were soon recognized (Adelstein 2010; Williamson 1994, 4;Valverde 2005, 24).

Thus, by ignoring the presence and condition of plastic negatives in photographic collections, the risk of loss of such valuable heritage is tremendous.

Over time, the ephemeral nature of cellulose esters film-based negatives became one of the most challenging issues for manufacturers, photographers, scientists, conservators, and overall caretakers that strive to foresee the decay of those negatives and to develop conservation solutions for the object itself. Consequently, caretakers and science conservators invested in the development of preventive measures to mitigate risk of cross-infection of entire collections caused by the release of acidic products resulting from the decay of cellulose esters (Norris and Gutierrez 2017). Among other tasks encompassing preventive measures for photograph collections (e.g. surveying and cataloguing), identifying and assessing of plastic negatives are crucial steps to safeguard film negatives. Furthermore, this is the starting point for decision-making processes regarding storage materials, duplication, rehousing conditions and conservation treatments (Fischer and Robb 1993, 117). Moreover, long-term preservation relies on monitoring the objects as well as the collection. In the absence of implementing and executing a preservation plan in which the tasks aforementioned are integrated, the risk of a total loss of collections is inevitable and can lead to catastrophic losses (Lavédrine 2000b, 135).

[1] James M. Reilly was Director of the Rochester Institute of Technology (RIT), and founder and director of the Image Permanence Institute (IPI).

However, these tasks are challenging due to the nature of such objects. Besides, these tasks are extremely difficult to perform when considering the large presence of cellulose ester film-based negatives in photographic collections; particularly, when considering that when there are no identification marks or visual signs of degradation, cellulose ester films might be indistinguishable (Fischer 2012, 1).

Thus, how is it possible to save millions of negatives? And where to start? What are the costs involved in the long-term preservation of valuable and unstable materials such as cellulose ester films?
The awareness of the historical value of photographic materials and the consciousness of their fast decay became a concern:

> *Whether in cinema, still, or microfilm form, the permanence of cellulose ester photographic film is an issue of tremendous cultural and financial significance. Much of the concern has been with the chemical stability of plastic film support* (Adelstein et al. 1992, 336).

With the aim to saving film collections, investigations were launched initially by producers, such as Eastman Kodak Company and Agfa-Gevaert Inc. (Ram 1990; Brems 1988) and later by research units such as the Centre for Polymer Stability at Manchester Polytechnic in the United Kingdom, the Centre de Recherche sur la Conservation des Collection in France and the Image Permanence Institute (IPI) in the United States of America (Reilly 2010a, 575; Adelstein et al. 1992; Allen et al. 1987; Louvet 1994). The main goal was to gather more information about the composition and decay of cellulose ester photographic films. The results obtained supported (and still support) the definition of preservation strategies for film collections and active conservation methodologies that were progressively tested and implemented.
In general, the research carried out focused on the degradation mechanisms of cellulose nitrate and cellulose acetate supports (Allen and Edge 1988; Edge et al. 1990; Edge et al. 1989; Ram 1990; Brems 1988; Adelstein et al. 1992). The aim was to understand the chemical and physical decay of those films and its relationship with storage conditions (temperature, relative humidity and moisture content, film containers and enclosures). Thus naturally aged and artificially aged films were analysed with the goal to estimate the lifetime of such objects under different archival conditions (Edge et al. 1988; Edge et al. 1990; Edge et al. 1992; Adelstein et al. 1992; Adelstein et al. 1995a; Edge et al. 1989; Lee and Bard 1988;Bigourdan 2006).
Simultaneously, determining the shifting moment (known as the autocatalytic point) from which cellulose ester negatives pass from the induction period to the irreversible degradation was also sought (Adelstein 2009, 3). Identifying the autocatalytic point is crucial not only for the object but also for risk mitigation. Therefore, in the 1980s and 1990s, research was carried out with the aim of detecting early stages of decay of still film negatives and moving picture film (Edge et al. 1992; Fischer and Reilly 1995;

Adelstein et al. 1995; Valverde 1997; Harthan et al. 1997). From those studies, commercial products (e.g. AD-STRIPS) were developed, becoming extremely useful tools for monitoring film collections (Fischer and Reilly 1995; Reilly 1993) (see Chapter 3).

Besides the development of test fields for detecting film decay, the studies performed in the last two decades of the 20th century were crucial for an in-depth understanding of storage conditions on the long-term preservation of plastic negatives. Considering the typology of film bases and a large number of specimens present in the collections, different ranges of temperatures and relative humidity were tested, concluding that low temperatures (cold and frozen storage, 4º and below 0º C, respectively) and low relative humidity (20% to 30%) extended the lifespan of cellulose ester film-based negatives by slowing down their degradation rate (McCormick-Goodhart 1996; Bigourdan et al. 1997; Adelstein 2009; Pigniolo 2004).

The contribution of enclosures for long-term preservation of film-based negatives was also researched (Bigourdan et al. 1998). The preservative and curative actions of enclosures were considered in experiments carried out, confirming that paper enclosures have a beneficial action by protecting the negatives from humidity, neutralising the acidic degradation products formed during the degradation process and allowing the escape of acidic gases (Bigourdan and Reilly 1997; Bigourdan et al. 1998; Lavédrine 2000b, 78). Hence, recommendations were given for joint implementation of proper enclosures[2] along with storage areas with climate-control (macro environment) in order to achieve an ideal long-term preservation for still film negatives (Bigourdan and Reilly 1997; J. Bigourdan et al. 1998; Bigourdan and Reilly 2000).

Regardless the beneficial effects brought by the implementation of cool, cold or freezing storage, the associated costs can vary and are not always a solution for institutions with a low budget, which face the inability to ensure the maintenance of the storage system (Wagner 2007; Daffner 2003). In addition, the effects of cold storage on composite materials, such as film-based negatives, raised some concerns due to the different shrinkage rates of the distinct materials present in plastic negatives (Shashoua 2004, 94).

Also, some active conservation methods have been tested. The deacidification of plastic negatives was one of the focus of some research in which the physical integrity of the object was kept (Johansen and Johnsen 2006; Silva 2009; Willet et al. 2015; Bigourdan et al. 1998). Other active conservation treatments were tested in which severely degraded CA or CN bases were removed (disposed of) in order to save the image layer (Munson 1997; Reed 2010; Pavelka and Naipavel-Heidushke 2005).

The dilemma of conserving of plastic negatives is therefore reflected on the dichotomy between preservation of the total object (base and emulsion layers) or keeping the emulsion layer when this is the only option. The former option indicates the efforts made over time to preserve this valuable heritage despite the cost associated with each action. As James M. Reilly wrote […] *photographs are physical objects as well as images* […] (2010a,

[2] Photographic enclosures should pass the Photographic Activity Test (PAT) according with the norm described in ANSI standard IT9.2-1988 (Lavédrine 2000; Fischer and Robb 1993).

570), however, sometimes options and priorities dictate how invasive should the interventions be.

The option for total disposal of the object, in particular for cellulose nitrate films, has been proposed (Calhoun 2010, 369). According to the literature, this option was considered only for extreme cases, specifically when it is impossible to safeguard the object and as a preservation action proposed to mitigate the risk of contamination of the collection (Fischer and Robb 1993). Over time, copying or duplication has been seen as a preservation option since it allowed to have access to the image and inhibited handling the original negatives (Calhoun 2010; Puglia 1989, 124). Initially, duplication was performed by contact printing of film-based negatives and gradually evolved to digitization (Puglia 1989). The effectiveness and low-cost process of digitization lead to its wide implementation. Unfortunately, duplication and digitization were frequently seen as justifications for the possible destruction of CN film-based negatives (Calhoun 2010, 369; Orraca 2010, 27). However, the management of analogue and digital copies were also shown to have an excessive cost and additionally digital files are susceptible to degradation or loss. Over time, the consciousness of the value of the original object increased due to photograph conservators' opinions such as José Orraca,[3] who defended the preservation of original photographic materials by saying,

> *However, and this is important, keep the originals!!* (J. Orraca 2010, 33).

In part, cold and frozen storage are currently the two existing options, which allow keeping the original negatives (degraded or not), avoiding further decay and preventing the risk of cross-infection of the collection. But, the implementation of such storage conditions requires financial investments. The implementation and execution of a monitoring plan are recommended to ensure the long-term preservation of film collections. It is also important to highlight that monitoring does not mean to look only for signs of degradation on the film but also guarantee and maintain a proper function of the equipment on which the ideal archival conditions (temperature, relative humidity and ventilation) for the storage rooms rely on. Even though, this seems to be a challenging task. As Peter Z. Adelstein (1995a, 288) wrote:

> *It is physically and economically unrealistic to monitor film collections for stability on a very frequent basis. There have been many examples of the film appearing in a very satisfactory condition in one inspection but being completely disintegrated in the subsequent inspections. Thus the ability to detect film degradation before it has progressed to an advanced stage has tremendous practical importance for the management of nitrate and acetate film collections.*

[3] José Orraca (1938-2009), one of the first photograph conservators, lecturer and founder the Photographic Materials Group of the American Institute for Conservation of Art and Historical Artefacts.

Therefore, on a practical basis, identification and macro assessment of film-based negatives are the two initial tasks performed in institutions through which it may be possible to ensure the safeguard of film-based negatives (Fischer and Robb 1993; Tolosa 2004).

However, how can archivists, conservators, librarians and collectors accurately identify and assess hundreds or thousands of film-based negatives?

It is true that field tests are extremely helpful to assess the decay of cellulose ester films. Nevertheless, the handling of these tests relies on the existence of a budget that covers testing materials as well as hiring properly trained conservation staff to install and evaluate the end results. As Nora Kennedy[4] (2010, 92) explained:

> *Many institutions with millions of photographs in their holdings and substantial support from in-house book conservators and paper conservators do not include even one conservator of photographs on their staff*.

The safeguard of photograph collections relies on the commitment, awareness and knowledge of other caretakers rather than photograph conservators.

Despite the similarities shared by paper, books and photographic materials, the diverse typologies, compositions and nature of cellulose ester films demand an in-depth knowledge to understand their specificities and unique nature. The lack of conservation staff to ensure the preservation of enormous quantities of film-based negatives is one of the issues that cultural institutions must face. Other concerns include the lack of proper conservation training and public unawareness of the existence and preservation challenges posed by millions of photographs present in public and private institutions.

Based on the issues presented here, it is possible to realize that the preservation of film-based negatives is problematic for several reasons. First, the chemical and physical behaviour of cellulose esters supports is considered the core of the problem. However, despite the awareness of the problems presented, the costs associated with the implementation of preservation strategies; the acquisition and installation of both storage equipment and enclosures and hiring specialized staff are equally challenging.

These issues are daily challenges on archives, libraries and museums that hold still film collections. Despite the useful information gathered and published, the diversity of film-based negatives and its degradation process complexity of cellulose ester films still demands further research and contributions.

As Mitchel Resnick[5] wrote:

> *Understanding something in just one way is rather a fragile kind of understanding*…[…] *Understanding something in several different ways*

[4] Nora Kennedy is the Sherman Fairchild Conservator in charge at the Metropolitan Museum of Art (MET), in New York, being responsible for the photograph conservation laboratory.

[5] Computer scientist, Professor of Leaning Research at the Massachusetts Institute of Technology (MIT).

> *produces an overall understanding that is richer and of a different nature than any one way of understanding* (M. Resnick as cited in Taylor 2013).

Additionally, as Orraca emphasized,

> *The object is of supreme importance. The function of a museum or library is to gather and preserve those items that fall within their interest or pursuit.* (J. Orraca 2010, 27).

Since plastic negatives were widely accepted, sustainability issues and preservation challenges are transversal to all photographic collections in which these photographic materials are present (Norris 2011). It is the mission and the responsibility of caretakers, photograph conservators, science conservators and civil society to safeguard such valuable heritage. It is the photograph conservator's mission to study and implement a holistic research that contributes to a deeper knowledge about the chemical and physical decay of film-based negatives that may support the creation and/or improvement of the methods used for identification, assessment, as well as for the definition of preservation strategies.

In order to understand if this international panorama is also verified in Portuguese collections, the next section focuses on the national context and the problems found in archives and collections of the country.

Cellulose ester film-based negatives in Portuguese photography archives: the will to preserve

Aiming to understand the present condition of film-based negatives resulting from the work of Portuguese photographers (amateur and professionals), four Portuguese archives were selected to study. The selection of the archives relied on their mission and on the existence of black-and-white cellulose ester-negatives collections dated back to the 1930s and up to the 1950s. It was decided to study objects from this period in order to avoid the first decades of production, which represent a more experimental period. Additionally, this timeline also avoids the possibility of finding negatives with polyethylene terephthalate supports, which are not the focus of this work. The selection of the collections relied on three main criteria: historical framework of the collection (dates, photography type, historical relevancy), film characteristics (support type, format, producers/brands) and present condition (conservation grades).

The Portuguese archives that fulfilled these parameters were: *Arquivo Histórico Ultramarino* (AHU), *Sistema de Inventário do Património Arquitectónico* (SIPA), *Arquivo de Documentação Fotográfica* (ADF) *and Arquivo Fotográfico da Biblioteca de Arte da Fundação Calouste Gulbenkian* (BA-FCG). These archives are physically located in Lisbon and hold collections produced during the first half of the 20th century. The plastic

negative collections held by these archives represent a broad type of support, formats, brands and uses.

The AHU archive[6] was legally created in 1931 with the aim to gather a wide typology of documentation related to Portuguese communities (mainland and overseas) and to preserve and disclose these documents to the public. The documentation held by the AHU archive is representative of the work done by several Portuguese researchers and photographers. Therefore, in part, AHU's photographic collection results from expeditions and researches performed in African countries such as Angola, Moçambique, São Tomé e Príncipe and Cabo Verde ("Arquivo Histórico Ultramarino," n.d.).

In the framework of this research, the AHU collection was selected due to its relevance for the study on the practice of photography overseas. Moreover, it is expected to understand the technical issues with which Portuguese photographers had to deal with during the expeditions in hot and humid climates in Africa. Coupled with this topic, it was also studied the methods used by Portuguese photographers to overcome the technical issues and climate adversities.

Figure 1.1 - Self-portrait of Elmano Cunha e Costa (left) and Priest Carlos Estermann (right). © DGLAB-AHU.

From the AHU archive, the Elmano Cunha e Costa (ECC) collection was selected based on the type of support (CN base), the exceptional condition and also due to the detailed description of the photographic technical work performed by the photographer in the 1930s.

In Fig. 1.1 a portrait of Cunha e Costa and his expedition partner Priest Carlos Estermann (1896-1976) is presented at Moxico region in Angola. In the framework of this study, the

[6] The AHU archive was under the Instituto de Investigação Científica Tropical tutelage until 2015 having transitioned in the same year to the Direção-Geral do Livro, Arquivos e Bibliotecas (DGLAB) (Decree-Law 148/2015, Serie I of July 2015).

information reported by Cunha e Costa was found to be relevant for the interpretation of the molecular assessment carried out. Moreover, regarding the practice of colonial photography, by studying the ECC collection it was possible to understand the working methods used at the time.

In a completely distinct perspective, the *Sistema de Informação para o Património Arquitectónico* -SIPA [7] archive was selected. From the several existing collections in the SIPA archive, the *Direcção Geral de Edifícios e Monumentos Nacionais* - DGEMN collection[8] was selected since it allows to fulfil the objectives of studying a collection with plastic negatives handled by different professional or amateur photographers, in which specimens with different formats and distinct brands can be found.

DGEMN's photographic collection results from the photographic survey of Portugal national trust. Besides the survey, it is also possible to find photo-documentation of conservation and restoration interventions carried out on classified monuments. In Fig. 1.2 an example of the photographic documentation carried out by DGEMN's technicians and photographers during conservation and restoration interventions executed on Portuguese monuments and sites is shown.

Figure 1.2 – Side façade of São Francisco church in Porto, Portugal, documenting an intervention performed under the supervision of DGEMN. © DGPC-SIPA.

[7] The *Instituto da Habitação e da Reabilitação Urbana* – IHRU was legally created by Decree-Law no. 223/2007, of May 30, and resulted from the addition of the attributions of the *Instituto Nacional de Habitação*, the *Instituto de Gestão e Alienação do Património Habitacional do Estado* and *Direção-Geral de Edifícios e Monumentos Nacionais* - DGEMN. In the context of this merger, IHRU, I.P., was responsible for the development and management of the *Sistema de Inventário do Património Arquitectónico* - SIPA, which was created in 1992 and includes a vast collection of information and documentation on Portuguese architectural, urban planning and landscape heritage. In 2015, the IHRU, and consequently the SIPA archive was transferred and integrated in *Direcção Geral do Património Cultural* - DGPC, pursuant to Decree-Law no. 102/2015, Diário da República no. 109/2015, Series I of 2015-06-05.

[8] One of the oldest heritage governmental services, formally created in 1929, pursuant to Decree-law nº 16791, Diário do Govêrno nº 97/1929, Série I de 1929-04-30.

This collection is the result of the work performed since 1929 and represents an extensive investment of the Portuguese governments on the preservation and disclosure of Portuguese national heritage.

The authorship of the photographs on this collection is vast, ranging between the institution staff members (architects, civil engineers and art historians) and works commissioned to professional photographers such as Domingos do Espírito Santo Alvão (1872-1946) e António Pedro Passaporte (1901-1983).

With the aim of disclosing all the documentation (photographs and paper documents) within the archive, in 1996 a mass digitization project was launched. In 2001, the physical centralization of the documents started by transporting and storing the photographic, administrative and graphic documentation coming from the regional archives in the facilities of *Forte de Sacavém*, a military fortress acquired to house the DGEMN collection.

The DGEMN collection was selected because it allowed studying CN film-based negatives with different formats. Additionally, the film-based negatives selected had already been surveyed and visually assessed, with conditions ranging from no signs of degradation to films showing signs of chemical decay.

As previously stated, the *Arquivo de Documentação Fotográfica* (ADF) was also selected to study. The ADF, formerly known as the *Arquivo Nacional de Fotografia*, was established in 1976 with the purpose of gathering, surveying, preserving and disclosing collections of Portuguese photographers. Under the tutelage of the *Direcção Geral do Património Cultural* – DGPC, this archive is also responsible for producing photographic documentation and managing the digital repository of national heritage images under the tutelage of national museums. The selection of the ADF archive relied on two reasons: its role in the preservation and disclosure of Portuguese photographs collections, and because it allows studying two collections from two professional photographers who had an active role in the Portuguese photography scene while working actively during the first half of the 20th century. The two photographic collections selected from ADF are the Manuel Alves de San Payo (SP) and Joaquim Silva Nogueira (SN) collections (Figs 1.3 and 1.4, respectively).

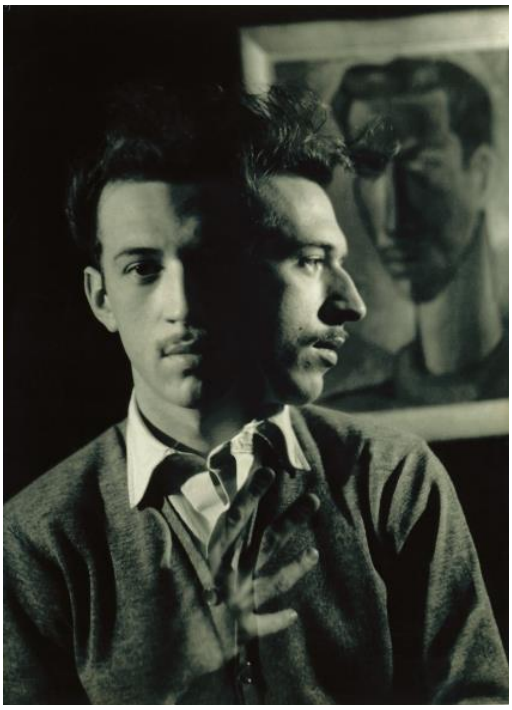

Figure 1.3 – Portrait of the artist and architect Nuno San Payo, authored by his father Manuel Alves de San Payo. © DGPC-MNAC.

Figure 1.4 – Portrait of the famous Portuguese fado singer Amália Rodrigues (1954), authored by Joaquim Silva Nogueira. © DGPC-ADF

Both photographers were responsible for their own photographic studios, where portraits had the greater expression in their works. Fig.s 1.3 and 1.4 are examples of portraits taken by the photographers Manuel Alves de San Payo (1890-1974) and Joaquim Silva Nogueira (1892-1959). These two collections were selected because, besides the survey, few conservation or preservation interventions had been carried out. Therefore, the film-based negatives from these two collections were in part in their

'primitive' condition, which allowed to see the photographer's original organization. Furthermore, in these two collections, film-based negatives with notch codes and producers embossed information was found. Additionally, it was easily identified the presence of CA based-negatives with a full range of degradation conditions and different formats. Nevertheless, the absence of degradation signs, led to questioning about the film typologies present in the collections. These issues reinforced the need of reviewing the methods currently used to carry out the identification and macro assessment of the collections.

Finally, from the *Arquivo de Arte* integrated in 2001 in the *Biblioteca de Arte da Fundação Calouste Gulbenkian*[9] (BA-FCG), a small set of severely degraded CN film-based negatives was selected due to the lack of similar examples in the collections aforementioned. This set of CN based negatives belongs to the Mário João Novais (1899-1967) (MN) collection. According to the information disclosed by FCG,[10] Mário Novais was also a renowned professional photographer, who established his photographic studio in 1933.

Figure 1.5 – Side façade of *Fundação Calouste Gulbenkian* (1969), authored by Mário Novais. ©BA-FCG.

Novais studio was specialized in works of Art photography, architecture, portraits, photo-reportage, advertising photography and commercial photography. Fig. 1.5 is an example of Novais photographic work for FCG. After Novais death, the resulting photographic collection of circa 50 years was acquired in 1986 by the FCG.

[9] FCG is a Portuguese private institution created in 1956 by Calouste Sarkis Gulbenkian. Located in Lisbon, among other objectives, this institution is focused on promoting knowledge by disclosing and preserving cultural heritage, investing in research in the science and education fields.

[10] Resulting from the M. Novais collection study and conservation treatment report presented in BA-FCG web page: http://www.biblartepac.gulbenkian.pt.

In conclusion, these collections hold more than 78.000 still film negatives, which are representative case studies for the issues addressed in this thesis:

a) Collecting information about the working methods used by Portuguese photographers in different production contexts (Portugal and African ex-colonies);

b) Identification of the assorted typologies of black-and-white film-based negatives used in Portugal in the first half of the 20th century;

c) Getting a realistic panorama of the current identification and assessment methods; conservation conditions of the film collections; and preservation strategies implemented in Portuguese institutions;

d) Identify degradation pathways;

e) Contribute for the improvement of identification and assessment methodologies and preservation strategies.

It is believed that in accomplishing the goals proposed, an important contribution will be given to the knowledge of photographic materials and photographic techniques carried out in Portugal between 1930's and 1950's. Hence, the results obtained in this research will contribute to improving the preservation of historical film collections in Portuguese institutions and the preservation of film collections present in archives and libraries worldwide.

Research goals and methodology

Considering the complexity of plastic negatives decay, the prime purpose of this work is to contribute for the definition of preservation strategies for black and white cellulose ester film-based negatives collections. This will be done by surveying the types of films present in the selected collections; analyzing the efficiency and reliability of identification and condition assessment strategies commonly used by the caretakers of film collections, and by providing new tools for the accurate implementation of preservation and conservation measures.

Taking as inspirational examples the insightful surveys of film-based negatives collections performed by David Horvath (1987), Betty Walsh (1995) and Jamie Jamison (2003), this research intends to be a starting point for a large survey of black and white still film-based negatives present in Portuguese photographic collections. As far as we know, this work is the first survey to be performed with the extensive support of

molecular assessment of cellulose ester film-based negatives held in Portuguese institutions.

This research aims to contribute to the discussion of decision-making processes and to provide more data that can support the identification and assessment of films as well as the preservation of film collections.
For that reason, a survey of Portuguese collections holding cellulose nitrate and cellulose acetate film-based negatives was carried out. It was decided to study collections showing plastic negatives with different film supports, assorted formats, distinct condition grades and different production contexts (professional and amateur, studio and documentary/field photography). For this study, three hundred and sixty-one film-based negatives were selected according to edge-printing and preservation condition. Based on the guidelines present in the literature (see Chapter 3), a five-grade condition chart was created for the selection of the cases studies.
Based on this approach, the importance of launching a discussion on the accurate identification and assessment of film negatives is highlighted as an urgent subject to be addressed, as evidence of erroneous identification and condition assessment were found (Chapters 3 and 6). This, as it is known, can result in catastrophic damages in this type of collection.
The molecular identification and assessment of naturally aged CN and CA still film negatives were also performed, as well as the study of innovative and non-destructive methods to assess the chemical and physical condition of the negatives. In this study the degradation mechanisms were not investigated. Nevertheless, whenever necessary observations were made about the possible mechanisms involved.
Finally, an artificial ageing test to follow the decay of the cellulose nitrate-based negatives under the influence of temperature and relative humidity was carried out.
As a result, this work intends to provide accurate tools for conservators, archivists and librarians, working with film collections in archives and museums.

Outline of the thesis

Chapter 1 – General Introduction

The topics addressed in this chapter support the discussion of sustainability issues of film collection preservation, which features the diversity of film bases, the broad production, techniques, as well as huge quantities of films which are a daily challenge for public and private institutions. In context, the scope and aims of this study is a brief description of selected archives and collections.

Chapter 2 – **State of the art**

This chapter includes a brief historical context of the invention, production methods and CN and CA polymers properties. Additionally, it presents a contribution to the knowledge of multi-layers structure of cellulose ester-films composition. An overview of degradation mechanisms of cellulose esters films is also discussed to allow for a wider understanding of the specificities of each type of film supports decay.
This chapter sustains the reading and discussion presented in the following chapters.

Chapter 3 - Currently used methods for identification and assessment of degradation of cellulose ester photographic negatives and motion picture film: an overview

A critical review of the currently used methods for identification and assessment used in the field of conservation of photographs and motion picture film can be found in this chapter. A summary of the different analytical techniques recently used to identify and characterize cellulose esters in the field of conservation of photographs is also given, as well as in the field of plastics conservation.

Chapter 4 – Preservation of film-based collections in Portugal: results of a national survey

To contextualize the aims of this study, a brief historical context of the use of film-based negatives in Portugal is given to introduce the current preservation panorama of Portuguese archives and collections. Chapter 4 discusses the results of a recent survey of Portuguese caretakers responsible for the preservation of film-based negative collections held by Portuguese institutions (public or private). Its purpose was to assess the current condition of cellulose ester film-based negatives in Portuguese collections, what methods are being adopted for identification and assessment of those negatives, as well as preservation strategies implemented in the institutions. This chapter reinforces the objectives and importance of the present work.

Chapter 5 – Experimental

In this chapter, broadly, three main topics are presented: methodology, description of historical negatives selected as well as samples samples prepared for artificial ageing, and instruments and methods. For start a description of the methodology established for this work is presented, showing the criteria for selection as well as the parameters established for assessment of the samples analysed in this study. A summary of the amount, typology and condition of films selected per collection is given. Concerning the artificial ageing, full description of the samples as weel as the chemical processing carried out is presented. Finally, intruments and methods used for film and image layers assessment is presented.

Chapter 6 - Case studies: naturally aged black and white cellulose esters film-based negatives from Portuguese collections

In this chapter, the chosen collections are described, and the results of the survey and visual assessment are given. Furthermore, the molecular identification and assessment of CN and CA film-based negatives from five Portuguese photographs collections are presented and a discussion of these results is given in which data collected is correlated with the nature of each collection, formats and brands.

The conservation condition of the selected negatives is discussed based on, visual assessment, infrared spectroscopy, Raman spectroscopy, pH and hardness (Shore A). A discussion concerning effective and non-effective relationships between molecular data and the visual assessment is also presented, providing new insight on identifying the most accurate methods used by the holders of this type of collection.

Chapter 7 - General conclusions and future perspectives

The main conclusions are presented, as well as future perspectives on preservation strategies of film collections.

Chapter 2
State of the Art

Chapter 2 – State of the art

2.1 Historical framework of cellulose ester film-based negatives – from the early days to the 1950's

2.1.1. Cellulose esters: the debutant plastics

For centuries man used natural polymers to develop a wide variety of objects for decorative and commodity items (Williamson 1999, 3). However, in the 19th century, the increasing search for natural polymers led to its sparse supply and consequently, they became more expensive (Böckmann 1907, 1–7). The necessity to supply industry with new materials made it possible to produce and replace objects made with natural polymers, hence cellulose esters[11] were invented (Shashoua 2008b, 21–22). The versatility of these semi-synthetic polymers, at the time known as new plastic[12] materials, provided an extensive application, thus becoming industrially competitive (Shashoua 2008b, 40).

Cellulose esters or cellulose derivatives are obtained by chemically treating natural polymers such as cellulose with a mixture of acids in a so-called esterification reaction (Hamrang 1994, 2; Shashoua 2008a, 40–42) (see section 2.2). Broadly, two cellulose esters were produced: cellulose nitrate (CN) and cellulose acetate (CA) by order of appearance (Hamrang 1994, 3; Stewart 1997, 4). The manufacturing process and the chemical properties of the CN and CA products dictated their applications[13]. In section 2.2 details are presented on CN and CA composition and manufacture.

The first attempts to produce a cellulose derivative were performed in the 1830s. From the range of CN products manufactured overtime, *Collodion*[14] and *Celluloid* were two of the most commercially successful CN products (Reilly 1991, 146). In part, the success of those products was accomplished with its use as a photographic emulsion and film base, respectively.

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[11] See section 2.2.

[12] The term plastic is applied to semi-synthetic or synthetic polymers (materials with a high molecular weight) produced through chemical reactions and modified by addition of additives that will improve the properties of the polymer itself and allowing their manipulation in order to produce new products such as films, fibres, coatings/lacquers, bulk and foams, etc (Shashoua 2008a, 1).

[13] The designations mentioned and others such as *Nitrocellulose*, *Nitrated cotton*, *Pyroxylin*, *Gun-cotton, Gunpowder* or *Smokeless powder* and were generically given to the compounds resulting from the nitration process (Worden 1911a, 568–782; Reilly 1991, 147; Shashoua 2008b, 237) (see section 2.2.2.). Nitrocellulose is the generic designation given to compounds obtained from the chemical treatment of cellulose with a *mixture of concentrated nitric acid and sulphuric acid* (Reilly 1991, 147). *Pyroxylin* is the term applied for cellulose nitrate soluble in ether-alcohol mixture (Field 1893, 140). The terms *gun cotton*, *gunpowder* and *smokeless powder* are generically used to refer cellulose nitrate but correctly should be used to refer highly nitrated and flammable CN compounds, e.g. propellants or explosives (Fernández de la Ossa et al. 2011; Shashoua 2008b; Reilly 1991; Barsha 1954).

[14] *Collodion* is described as a solution of cellulose nitrate or nitrocellulose (guncotton) in alcohol and ethyl ether (40/60) (Reilly 1991, 150). *Collodion* is also the designation for the photographic emulsion invented by Frederick Scott Archer (English, 1813-1857) in 1851 (Osterman and Romer 2007, 31).

After the initial start-up in Europe, in 1907 a successful production of CN was performed by the Hyatt brothers[15] (Reilly 1991). Unlike the English producers Alexander Parkes (1813-1890) and Daniel Spill (1832-1887), the Hyatts understood the benefits of using camphor as a CN plasticizer. The Hyatt's production process relied on heat and pressure to blend camphor and pyroxylin[16]. From this production method a final product which is known as *Celluloid* was obtained (Worden 1911a, 580–82). By finding that camphor acted as a CN's softer and solvent, they were able to reduce the quantities of solvents used in the production of CN. As a result, it was easier to remove the low amounts of solvents used and therefore to obtain *Celluloid*, with improved stability at lower production costs (Worden 1911a, 578, 580–82; Shashoua 2008a, 22). The Hyatt's achievement became crucial for the commercial production and moulding of plastics (Barsha 1954, 714). The physical and chemical properties of *Celluloid* allowed its application for the manufacture of a wide range of products such as cloths, paints, lacquers and commodity items. Moreover, film negatives and motion picture film were still regarded as examples of the uttermost successful applications of CN (Worden 1911a, 580–82).

Initially, produced in England and the United States of America, the satisfactory qualities of CN became increasingly appreciated, being later manufactured in other European countries such as France (1875), Germany (1878) and Italy (1910) (Hamrang 1994, 4).

Nonetheless, the high flammability and chemical instability of CN polymer lead to its gradual replacement by cellulose acetate (CA) (Shashoua 2008a, 24).

In 1865, CA was synthesized for the first time by heating cotton with acetic anhydride (Worden 1916a, 2530; Brydson 1999, 621; Krässig et al. 2012, 353). After several attempts, a successful full esterified product was obtained by performing an acetylation reaction with (anhydrous) sodium acetate and sulphuric acid (catalyst) (Worden 1916a, 2532). Since then, sulphuric acid became the most common catalyst for acetylation reactions (Balser et al. 2012, 353). However, despite the improvements carried out, CA commercial production was restrained due to its limited solubility in less expensive solvents (Ballany 2000; Balser et al. 2012, 353).

In 1894, new developments in the industrial production of CA were accomplished by replacing the catalyst, sulphuric acid, by zinc chloride (Malm and Hiatt 1954, 769,782). From this acetylation process a fully esterified CA, a cellulose triacetate (CTA), was obtained (Worden 1911a, 2537). The German chemist Hermann Ott (1852-1931) compared the action of sulfuric acid and zinc chloride, concluding that the esterification with sulfuric acid was more efficient since it required a lower volume of the catalyst to perform the reaction at mild temperature conditions, in opposition to the reaction with zinc chloride (high volume of catalyst and high reaction temperatures). Despite this accomplishment, the exclusive solubility of CTA in chlorinated solvents was inconvenient for commercial production due to the expensive costs of the solvents. Moreover, it was found that zinc chloride inhibited acetic acid's recovery thus increasing the production costs (Malm and Hiatt 1954, 782). These disadvantages caused financial constraints and

[15] John Wesley Hyatt (1837-1920) and Isaiah Wesley Hyatt (1827-1904), two North America inventors.

[16] Pyroxylin was already described. See footnote 3.

delayed commercial production of CTA. In 1904, an alternative was found by performing a partial hydrolysis of CTA (primary acetate) and obtaining a soluble cellulose acetate known as cellulose diacetate (CDA) (Worden 1916a, 769; Balser et al. 2012, 353).
Comparatively, with the previous CA production methods, CDA's production was less expensive and commercially more competitive due to the use of affordable solvents such as acetone. Moreover, changes in acetylation reaction (e.g. lower temperatures and a higher rate of evaporation of the solvents) also allowed for a decrease in manufacturing costs (Worden 1916b, 2553). Comparatively, with CN polymer, CA was considered more stable and less hazardous. These properties led the plastic industry as well as the photography industry to recognize the commercial opportunity to produce mouldable objects and film-based photographic negatives with CA and replacing CN (Shashoua 2008a, 42).
Despite its non-flammable nature, CDA instability was detected, being shrinkage and acidification (the characteristic vinegar odour) two important degradation signs pointed out (Horvath 1987, 4).
Later, with the discovery of other production methods (see section 2.2.3), it was possible to produce CTA industrially. Furthermore, two other CA derivatives or also called mixed esters of cellulose were produced, the cellulose acetate butyrate (CAB) and the cellulose acetate propionate (CAP).
The use of CA's polymers depended greatly on their chemical and physical stability. Over time the negative's base was gradually replaced depending on their properties and their suitability for each type of photographic film. In the following section, a chronology of the production and use of cellulose esters as a film base for photographic negatives is presented. Furthermore, details on the composition, production methods and properties of the cellulose ester film-based negatives are also given.

2.1.2. The contribution of cellulose esters for a new era of still photography

As previously stated, the advent of cellulose esters was crucial for commercial production of plastics and subsequent application to manufacture a wide range of products such as cloths, paints, lacquers, commodity items and especially for the invention and development of photographic negatives and motion picture film. Given the significant role played by these polymers for the development of still photography, in this section, a brief review of the more relevant historical and technical aspects is presented.

The birth of photography is firstly marked by the desire of obtaining detailed images of 'reality', followed by the strong intention of performing multiple reproductions of that same image (Romer 2007, 25).
Initially, photographs were unique images, with opaque supports (e.g. heliography, daguerreotypes and tintypes), which were impossible to reproduce or print (Osterman

and Romer 2007). In a few decades, these photographic processes were gradually replaced; first by paper negatives, followed by glass plate negatives and lastly by plastic negatives (Osterman and Romer 2007; Valverde 2005). The progressive replacement of the negatives supports, the invention of the gelatine-silver bromide photographic emulsion[17] (Valverde 2005, 14) and the development of new cameras (Fig. 2.1) were very appreciated by the public mostly because it demanded little photographic skills and no preparation of the materials by the photographers. Technically these improvements shaped photography and lead to the rise of amateur photographers (Ward 2008, 440; Simmons 2008). The gelatine-silver bromide photographic emulsion medium was used for the commercial production of ready-to-use photographic negatives, such as plastic negatives. Regarding the gelatine's chemical and physical stability, more information is given in section 2.3.1, pages 53 to 55.

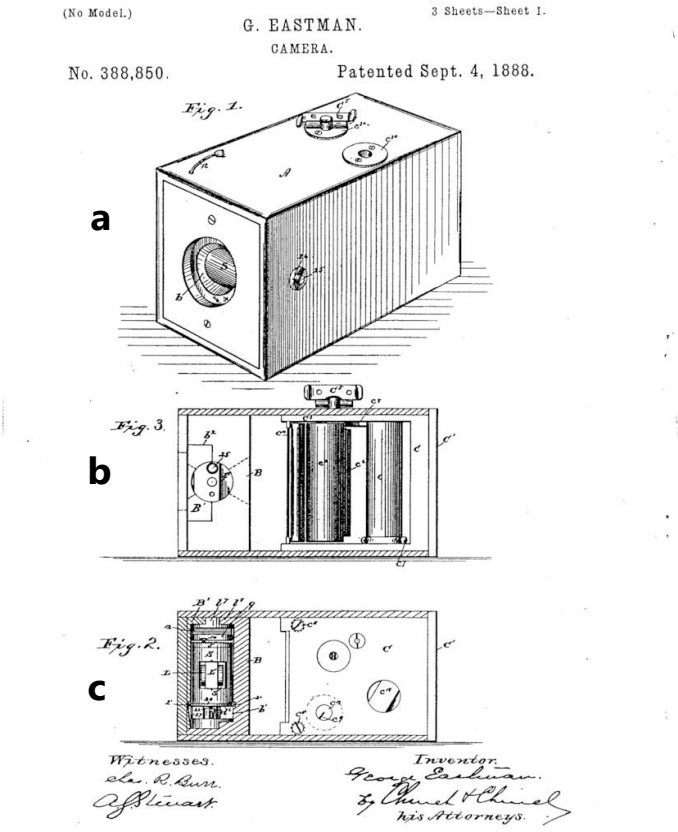

Figure 2.1 Photographic camera patented by George Eastman in 1888. Top: view in perspective of the complete instrument (a). Middle: top view of the camera (b). Bottom: side view of the instrument (c) (adapted from Patent nº 388,850).

[17] The gelatine silver-bromide photographic emulsion was invented by the British physician and photographer Richard Leach Maddox (1816-1902) and replaced albumen and collodion photographic emulsions. Since its invention, gelatine-silver bromide emulsions have been widely used (Valverde 2005, 9–18). The success of gelatine emulsions relied in part on its chemical stability towards processing solutions (Neblette 1952b, 118). Technically, gelatine proved to be an excellent photographic medium by allowing the decrease of exposure times to fractions of seconds.

As previously mentioned, the industry of photography and photographers desired to have transparent supports through which it could be made possible to capture an image and secondly to reproduce multiple and sharp prints of it. It was believed that photographic negatives with light and flexible supports would also improve the photographer's activity. With that in mind, in 1885 the North American George Eastman[18] (1854 – 1932) produced the first flexible and rollable photographic negatives, designated as *Eastman American Film* [19] (Adelstein 2010, 384; Pavão 1997, 44). Eastman's first rollable negatives were composed of paper supports and gelatine-silver bromide photographic emulsions (alum hardened) (Osterman and Romer 2007, 78; Pavão 1997, 44). Thus, despite the recognized flexibility, those negatives were still lacking transparency. To overcome the drawbacks of paper supports the gelatine emulsion was peeled from the paper support and transferred, which obtained a 'transparent film' (Osterman and Romer 2007). The return to paper supports was in part a setback since professional and amateur photographers had already enjoyed the transparency of glass supports. Additionally, the gelatine's peel off process was a hard and risky task. Therefore, consumer interest and an increasing market stimulated the industry of photography to find a new material that gathered transparent and flexible properties.

Being aware of the advent of plastics, the successful replacement of paper and glass supports happened when the industry of photography employed cellulose esters[20] to create plastic negatives or film-based negatives[21] (Adelstein 2010, 385). The selection of these materials relied on their optical, chemical, and physical properties (Adelstein 2010, 385–90; Neblette 1952, 161; Williamson 1994, 1; Sata et al. 2004, 325). Table 2.1 summarises the properties demanded by film-based negatives.

The flexibility, transparency, lightness and toughness of these materials proved to be extraordinary advantages for the manufacture of film-based negatives (Adelstein 2010, 385–90; Neblette 1952c, 152). Additionally, the successful compatibility of cellulose ester bases with the gelatine emulsion commercially placed plastic negatives as one of the most appreciated photographic materials. The success achieved by introducing cellulose esters as a base for photographic negatives satisfied the manufacturers and the public in general. The wide recognition of the extraordinary properties of cellulose ester film-

[18] Entrepreneur, founder of the Eastman Kodak Company.

[19] The *Eastman American Film* was produced between 1885 and 1889 (Pavão 1997, 44). This process was preceded by the first transparent and flexible film invented by the Englishman Frederick Scott Archer (1813-1857) which consisted of a collodion emulsion which was removed from the glass negative holder and placed on a paper support (Osterman and Romer 2007, 77).

[20] Detailed information about the production of cellulose esters is given in section 2.2.

[21] The term 'Film', which in the mid-19th century was commonly used for identifying […] *a thin coating on a secondary support* […] (Osterman and Romer 2007, 77) or more precisely a photographic emulsion. However, over time and with introduction of flexible and thin bases the term assumed another character and become the designation for film-based or plastic negatives (Osterman and Romer 2007, 77).

based negatives led to an enormous transformation and growth of the industry of photography (Adelstein 2010, 385).

Table 2.1 Technical requirements for film supports (Adelstein 2010, 388; Nebblete 1952, 161; Williamson 1994, 1; Sata et al. 2004, 325)

Film Properties	Technical Requirements	Remarks
Optical	Transparency, optically homogeneous, without visible imperfections, colourless	Requested for printing
Mechanical/physical	Flexible, strong, dimensionally stable, with tensile strength; no curling or buckling, elastic and plastic	Requirements for use in cameras and cinema projectors.
Chemical	Stable; moisture resistance; resistance to photographic developing solutions; compatibility with the emulsion layer (inert and provide good adherence)	Essential request for preventing distortion and chemical processing (development)
Thermal	High softening temperature, low flammability	For archival storage
Static	Low charging capability	To reduce dust attraction
Solubility	Soluble in non-toxic solvents	For production by solvent casting

Cellulose nitrate or celluloid was the first plastic to be used as a base for photographic negatives. The properties previously mentioned prove to be extraordinary advantages for film base production, leading to a progressive appreciation of celluloid and to an enormous transformation and growth of still photography and the invention of the motion picture industry. Due to its high flammability, from 1923 until the 1950's, CN was gradually replaced by CDA, CAB and CTA (Adelstein 2010, 385–90; Valverde 2005, 19–27).

Table 2.2 summarises the timeline of production and use of cellulose esters film-based negatives.

Table 2.2 CN and CA film-based negatives timeline of production (earliest and latest dates), formats, film type and producers (Fischer and Robb 1993; Valverde 2005; Eaton et al. 1985; Calhoun 2010)

Esters film base type	Dates	Film type	Producer
CN	1890 - 1933	X-ray	Kodak
	1890s - 1938	Roll film in size 135mm	Kodak
	1890 - 1939	Professional portrait and commercial sheet film	Kodak
	1890 - 1942	Aerial film	Kodak
	1890s - 1949	Film pack	Kodak
	1890s - 1950	Film rolls (616, 620, 828, etc.)	Kodak
	1890s - 1951	Professional motion picture (35mm)	Kodak
CDA	1923-1955	Roll and sheet	Agfa, Ansco, Dupont, Defender, Kodak
CAP	1927-1949	Roll	Kodak
CAB	1936-today	Sheet, X-ray, aerial maps	Kodak
CTA	1950 -today	Roll	Probably all manufacturers indicated

Tailored film-based negatives for amateur and professional still photography, movie picture, as well as for X-ray and aerial photography were manufactured to meet the public's request and vast needs (Valverde 2005, 20,24). Plastic negatives were industrially produced with standardized thickness as well with photographic emulsions with tailored light sensitivity (isochromatic and panchromatic emulsions[22]), responding to different technical demands (Lavédrine 2008; Valverde 2005, 19–27). Table 2.3 summarises the correlations between film type, format (and thickness) and the technical requirements for each type of film.

[22] For more information see Appendix I

Table 2.3. Type of films according to its use and films requirements (Nebblet 1952, 161)

Type of film	Requirements	Remarks
Amateur roll film	Thin base	To allow winding on a spool
Film Packs	High flexibility	To prevent damage *when the tab is pulled*
Motion Picture Film	High strength and toughness, dimensional stability	To resist the traction of the mechanical teeth
Sheet Films for Portraits or commercial use	Flat under all atmospheric conditions, thicker base	To remain the focal plane

Film-based negatives are complex assemblages of various materials, each one of them with different chemical and physical properties (more information is given in section 2.3). An extraordinary evolution of photography was seen during the late 19th century and the beginning of the 20thcentury mostly due to the development of cellulose ester film-based negatives.

While in the early- and mid-19thcentury photography was an arduous task, relying on the scientific background and photographic skills of the photographer, in the last quarter of the 19th century the breakthroughs allowed for a simplification of the practice of photography (Simmons 2008, 30). The massive industrial and commercial production of film-based negatives, along with the production of small cameras and commercial production of processing solutions shaped the industry of photography and the perception of 'taking photographs' (Ostrow 2007; Garner 2007). Therefore, the conditions for a democratic use of photography were gathered, leading to an increased use of film based-negative by professional photographers and consolidating the use of such materials by an even broader public, the amateur photographers (Garner 2007). These new consumers triggered large-scale production in the photography industry (Simmons 2008, 32).

Despite the increasing industrial production of the still film, several changes were seen in the 20th century as to production quantities and use of each type of cellulose ester base (see Table 2.2). After the successful introduction and outstanding acceptance of CN film base, a decline in the use of these types of supports was advocated mostly due to chemical instability and fire hazards (Adelstein 2010, 385). Consequently, in 1951 the Kodak Company discontinued the production of CN bases (Valverde 2005, 20). These drawbacks lead to the replacement of CN by CA polymer (Valverde 2005, 24). Initially, the industry of photography started by replacing CN supports with cellulose diacetate (CDA) (Table 2.2). However, CDA's poor physical and chemical properties were early detected. With the aim to overcome the disadvantages of CDA, in the 1920's the chemists

H.T. Clarke[23] and C.T. Malm[24] from Eastman Kodak Company initiated the production of cellulose mixed esters, CAP and CAB (Adelstein 2010, 389; M. F. Valverde 2005, 24). CAP was the first cellulose mixed ester to be produced in 1927, being used until 1949 as film support for amateur motion picture (Adelstein 2010, 389; Valverde 2005, 24) (Table 2.2). However, CAP lacked toughness and strength properties, necessary to replace CN bases used in motion picture film (Adelstein 2010, 389).

Concerning CAB, the non-flammability and dimensional stability advantages of this polymer showed that it was suitable for replacing CN bases. Therefore, between 1936 until circa 2000s professional sheet, aerial film and X-ray film were manufactured with CAB base (Adelstein 2010, 389; Valverde 2005, 24) (Tables 2.2 and 2.3).

Nevertheless, a substitute with the required mechanical properties for replacing the CN base used in motion picture film was still lacking. It was found that CTA had the desired mechanical properties according to research carried out before and after World War II (WWII). Nevertheless, as previously said, the production costs were high and restrained industrial production of CTA (Adelstein 2010, 389). The problem was solved by discovering a proper solvent with which it was possible to produce CTA (Adelstein 2010, 390; M. F. Valverde 2005, 24). In 1947, Kodak introduces CTA as film support for motion picture film due to its recognized strength and dimensional stability. Later in 1951, Kodak discontinues the manufacture of CN films (Valverde 2005, 24; Adelstein 2010, 390) (Table 2.2).

As presented in Table 2.1, since the last decades of the 19th-century cellulose esters have been predominantly used to produce film-based negatives. The chemical and physical properties of these plastic negatives empowered the photography industry to produce versatile and tailored products that led to its wide use, nowadays present in film archives all over the world. Moreover, as briefly explained, cellulose ester film-based negatives are currently a major concern for all the conservators, archivists, librarians, curators and collectors, who are responsible for the long-term preservation of such valuable and ephemeral heritage.

2.1.3. A brief overview of the production of cellulose esters still films

The quality and stability of plastic negatives relied on the chemical and technological developments carried out since the last decades of the 19th century and throughout the 20th century. The straight correlation between production methods and degradation of plastic negatives is of extreme importance for an in-depth understanding of degradation pathways and further preservation of the objects and collections. Thus, a brief overview

[23] Organic chemist at the Department of Synthetic Chemistry Research Lab, from the Eastman Kodak Company, Rochester, New York.

[24] Chemical engineer, Superintendent of the Cellulose Acetate Development Division of the Eastman Kodak Company, Rochester, New York.

of the production methods used to commercially produce cellulose ester still films is presented in this section.

In the early years celluloid film production relied on the efforts and skills of photographers. Incapable of producing CN base, the photographers bought from CN producers' celluloid sheets on which they coated a photographic emulsion (Adelstein 2010, 385).

The first attempts to produce photographic negatives with CN sheet were performed in the early 1880's by the French photographers David and Frontier. In England, Colonel J. Waterhouse made similar attempts (Harding 2008, 1207). All found that the production of photographic negatives with CN sheets was more expensive than with glass supports. CN producers also considered that the production of thinner and transparent films was not commercially advantageous (Harding 2012, 2-3).

The innovative invention of commercial CN films happened in the late 1880's when John Carbutt (1832-1905)[25] challenged Hyatt brothers to invest in the production of thin celluloid films. From the joint efforts resulted the commercial production of *Carbutt's Flexible Negative Films,* which consisted of thin sheet films coated with a silver-gelatin emulsion (Hager 1983, 3). Carbutt's knowledge on the production of dry plates allowed him to be the first to commercially produce CN sheet films in the United States of America (Valverde 2005, 19; Adelstein 2010, 385) which were exported after to Great Britain (G.B.) (Harding 2012a, 7). Shortly after Carbut's introduction of flexible films on the English market, the British companies Wood and J. D. England announced their own production of celluloid films (Harding 2012a, 7).

Despite the innovative breakthrough, Carbutt's films were rigid and inhibited the massive production of roll films (Harding 2008, 1). In 1887, Hannibal Goodwin (1822-1900)[26] filed an application for the patent *Photographic Pellicle and Process of Producing Same* describing the production process on how to make a continuous long flexible film (Goodwin 1887). In 1889 this patent was recognized, as well as another one from Kodak which has the same aim: to produce a transparent roll film (Reichenbach 1889). At that time, both producers started a legal battle for the rights to produce a film which ended in 1914 (Adelstein 2010, 385).

The interest on CN film-base negatives evolved in the 1880's. Manufacturers invested in scientific research and technological improvements to overcome the initial drawbacks found in its production and to develop high-quality products at a lower cost (Hager 1983, 3; Siemann 2005, 130:1–2).

Early producers understood that the chemical and physical properties of CN bases depended on the rate of evaporation of the solvents used to dissolve CN dopes, e.g. the formation of bubbles in the films caused by fast evaporation of solvents (Worden 1911b;

[25] Pioneer photographer, inventor and producer of dry plate negatives and X-Ray technology (Wisniewski 2008, 271).

[26] Hannibal Williston Goodwin was a North American Episcopal priest and entrepreneur.

Adelstein 2010; Hager 1983). Furthermore, celluloid brittleness was associated with the use of *wood alcohol*[27] (Adelstein 2010, 385).

Henry M. Reichenbach[28] overcame the initial drawbacks and improved the quality of CN products by performing the dissolution of CN dopes with a solvent mixture of wood alcohol, camphor, amyl acetate and fusel oil[29], thus enhancing new methods for CN's production (Adelstein 2010, 385). By using fusel oil it was possible to control the rate of solvent evaporation, and in the end improve the properties of the films. Furthermore, it was also found that fusel oil decreased the adhesiveness of celluloid (Worden 1911a, 736). Thus, it was possible to prevent opalescence and pitting of the films during the drying process and so getting a final product with improved stability and clarity (Worden 1911b, 847).

Reichenbach's celluloid films production was indicated by Edward Chauncey Worden[30] as the most suitable to control the viscosity of the dopes and to obtain improved properties for film base (Worden 1911b, 839; Adelstein 2010, 835).

Throughout the history of the production of CN film-based negatives, chemical and technical improvements dictated the commercial success of these materials.

By reviewing monographs from the first half of the 20th century in which the history, chemistry and production of cellulose derivatives are the core subjects (Worden 1911a; Worden 1916b; Ott et al. 1954), it is possible to understand the wide variety of formulations and production methods tested and used over time.

Apart from the chemical production of polymers and products made with those, developments in technology also contributed to improve the production quality of the films.

The most remarkable technological improvements can be summarized in three production methods: the 'batch-type or discontinuous casting', the 'continuous film casting' and the 'solvent cast process' (Adelstein 2010, 385–87; Siemann 2005, 130:1–2).

Initially, CN film-based negatives were produced with the 'batch-type process' (Worden 1911b, 839; Adelstein 2010, 385) which consisted of pouring CN viscous solution on a polished plate glass casting table (Worden 1911b, 839; Osterman and Romer 2007, 60). In Fig. 2.2 an example of a casting table is presented.

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[27] Wood alcohol (CH_3OH) is an optional designation for methyl alcohol or methanol (Osterman and Romer 2007, 39). The designation was applied due to the fact that in old times methanol was produced by the distillation of wood.

[28] Henry M. Reichenbach (- 1916) was a chemist hired by George Eastman to work at the Eastman Dry Plate Company of Rochester, N.Y., U.S.A., for the specific purpose of investigating and discovering a method for economically producing flexible roll film.

[29] Mixture of volatiles, oily liquids resulting from alcoholic fermentation, which contain amyl-alcohol ($C_5H_{11}OH$), n-propyl ($CH_3CH_2CH_2OH$) and isobutyl ($(CH_3)_2CHCH_2OH$) alcohols.

[30] Worden (1875 – 1940) authored monography and compendiums focused on the history, production and application of cellulose esters.

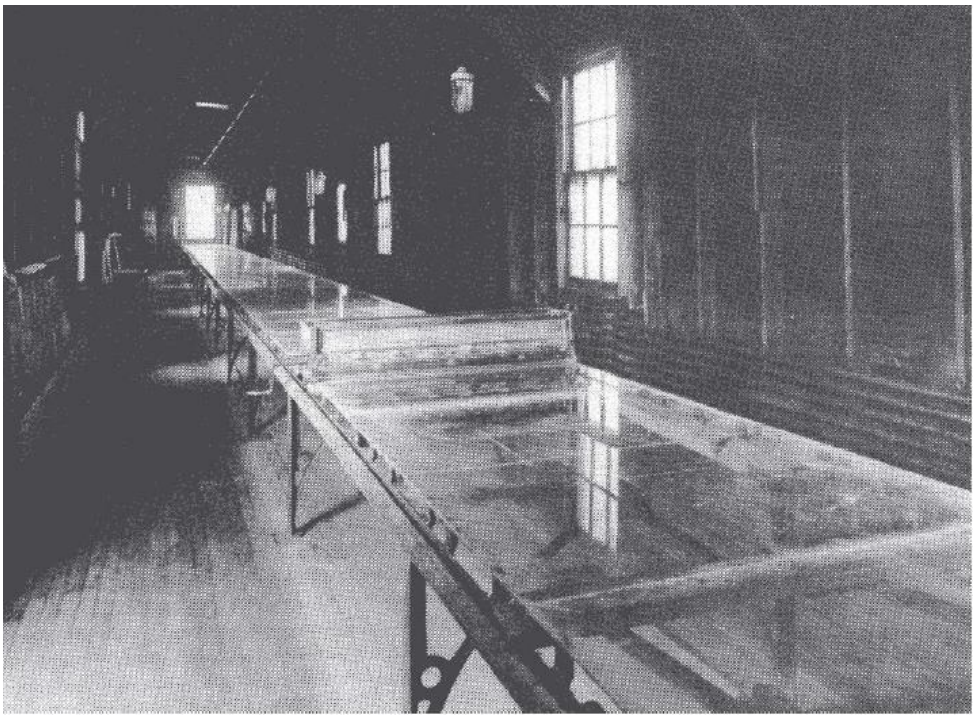


Figure 2.2 - General view of an early CN production room and an example of a casting table. ©Ryerson University Archives.

The 'batch-type process' was used for ten years being replaced by the 'continuous film casting process'[31] (Adelstein 2010, 386; Siemann 2005, 130:1–2). The *Celluloid Company* in 1896 and the *Eastman Kodak* in 1901 implemented the 'continuous film casting process' production technology (Siemann 2005, 130:1). In the 'continuous film casting process', the glass tables were replaced by rotating cylinders with a peripheral surface on which the viscous solution was poured. With this production process continuous strips of film were obtained (Adelstein 2010). Later Kodak accomplished another breakthrough by developing new equipment which was described as a […] *wheel with 20'' wide and 9' in diameter, which the dope from a hopper was poured. The wheel was turned, hot air evaporated the solvent, and the film base was stripped from the wheel after one revolution* […] (Adelstein 2010, 386). Despite the success reported with this *dope-casting* process, the films obtained showed imperfections (surface irregularities) that resulted from wheel corrosion caused by the solvents. Additionally, physical damages to the surface of the film could also result from the strong adhesion of the film to the hopper slot. Moreover, it was found that the solvents could stain the films (Adelstein 2010, 387). The European companies started some years later with the 'belt casting technology', which offered the advantage of speeding the production process. The main concerns with the 'belt casting technology' was the uniformity of the thickness and joints of the belts that could lead to irregularities in the films (Siemann 2005, 130:1). Agfa was the first European company to develop production with copper belts (Siemann 2005, 130:1). One of the main disadvantages of the continuous film casting process' and 'belt casting technology' was the lack of solvent recovery (Siemann 2005, 130:2)

[31] The first continuous casting machine was granted to T. H. Blair and S. E. Waterman in 1897.

Therefore, after more scientific and technical investments, the 'continuous film casting' process was upgraded to the 'solvent cast process'. The 'solvent cast process' consisted of […] *large polished wheels or endless moving metal belts, along with solvent curing sections, a solvent recovery system, and a highly sophisticated control equipmen*t […] (Adelstein 2010, 387). This technology allowed for producing films with uniformed thickness, excellent optical purity and orientation, and low haze (Siemann 2005, 130:1) The CN and CA film bases obtained with this process had improved in quality. The success of this method dictated its use to produce CA film bases.

In sum, among other properties, the film's transparency and flexibility were difficult to accomplish. Therefore, considering the high quality and tailored properties demanded for still film negatives and motion picture film supports, in the late 19thcentury some entrepreneurs saw the opportunity to financially invest in the production of those photographic materials. The first companies funded chemical and technological research that fostered new production methods and equipments. These investments launch the bases for the industrial production of plastics, considering that […] *celluloid inaugurated the advent of engineering plastics* […] (Selwitz 1988, 1). Thus 'the advent of engineering plastics', or more precisely the production of these plastics is linked to the evolution of production of photographic and motion picture film supports (Siemann 2005, 130:1).

2.1.3.1. Remarks on cellulose ester film-based negatives production in Europe

Under the framework of this research, it was considered relevant to search for more information about film-based negatives production in Europe since it may launch new perspectives on still film negatives stability and it may support the results obtained in this study.

To achieve this goal, four European institutions responsible for the preservation of historical documentation, related to the production of the photographic film, were contacted. The selection of those institutions relied on references of European film producers found in the literature (Pavão 1997; Harding 2012a; Harding 2012b; Peres 2007); and extensive readings of 'Encyclopedia of Nineteenth-Century Photography, Volume 1, A-I index' and 'Encyclopedia of Twentieth-Century Photography'. Based on the information gathered in the literature, the National Media Museum in Bradford, UK; Film Ferrania, in Italy; Bayer Archive, in Germany, and Agfa-Gevaert Archive in Lieven, Mortsel, Belgium were also contacted. Fortunately, Agfa-Gevaert archive conceived a visit, where some information regarding the production of CN and CA films was collected. Therefore, in this section, a summary of the information collected in the Agfa-Gevaert archive is presented.

When questioned about Gevaerts' production of CN film, the person responsible for the Agfa-Gevaert archive, Mr. Willy Van Leemput, explained that before World War I (WWI) Gevaert bought CN base to produce photographic negatives. According to him, at that time the Gevaerts' suppliers were the Société pour le Blanchiment des Textiles, Paris; Southern Chemical & Coton Company of America; and the 'home-suppliers' Peter

Temming; Hamburg-Glückstadt and Hercules Powder Company, Wilmington, Del. (United States of America). Additionally, between 1913 and 1920 Gevaert bought CN base to the Deutsche Celluloid-Fabrik, Eilenburg, from Germany, and to the American Celluloid Company (in Europe represented by Gulterman & Co., Ltd. London). The information confirms what was described above and indicates that in the 1910's and 1920's some producers were still not producing the necessary film base and thus buying CN blocks or CN film to several suppliers. It was also possible to survey the European and western CN suppliers[32] of CN stocks. Which resulted from an interview with Mr. Van Leemput, Table 2.4 shows information about Gevaerts film-based negatives production. This information was gathered in the framework of this study with the aim of establishing a chronology for Gevaert's commercial production of cellulose ester film-based and to contribute to a broader knowledge of film-based negatives production in Europe.

Table 2.4. Gevaert key dates on cellulose ester film-base negatives production

Dates	Remarks
1910	Start film production on bought base
1913	Start manufacturing cellulose nitrate
1922	Start manufacturing roll film
1928	Film on own CN bulk made
1929	Start production of amateur film on a purchased triacetate base
1930	Start manufacturing 24 x 36 mm film
1930	Launch research on CN and CA production
1934	Start manufacturing cellulose diacetate
1935	Start manufacturing cellulose triacetate
1948	Start manufacturing cellulose acetate butyrate
1949	Stop manufacturing diacetate
1950	Produces triacetate with quality comparable to cellulose nitrate; stop manufacturing cellulose acetate butyrate
1952	Stop manufacturing CN
1966	Volume climax on triacetate manufacturing
1967	Start manufacturing PET film base.

By comparing the information presented in Tables 2.2 and 2.4 it is possible to conclude that different producers were working on the same materials at different periods of time.

[32] Heckman (2010, 488) also addressed the issue of production and supply of CN and confirmed that *filmmakers* purchased CN raw stocks from multiple manufactures.

One of the most relevant information for the conservation field is that Gevaert stopped producing CN one year after Kodak, however, it is not clear if that was only for CN roll films or also sheet films (see Tables 2.2 and 2.4). Another issue of interest is the attention given about Gevaerts' purchase of CTA to produce an amateur film in 1929 and the starting date of his own CTA film in 1935 (Table 2.4). Following on from Nitrate to Safety film, these dates might point out to a period of research, technology and product development prior to a stage of CTA commercial exploitation (Enticknap 2002, 202). Moreover, according to the data presented in Table 2.4, Gevaerts CTA's commercial exploitation might have happened later in 1950. Nevertheless, it is also important to consider Enticknap's indication about the Nazi industry breakthroughs on CTA film base production in Germany (Enticknap 2002, 206–11). According to Enticknap, after WWII the Nazi's CA production methods to obtain film-base negatives triggered the Allies attention, especially North Americans and British enterprises and governments. In the end, the former won the dispute, being the first to get to the formulations and equipment related with the Methylene Chloride production process held in the I.G. Dormagen industrial facilities (see section 2.2.3). By gathering equipment and research documents the North Americans were able to industrially produce CTA film supports in the years that followed the end of WWII (Enticknap 2002, 206–11). This information is also reported in the *British Intelligent Objectives Sub-Committee Report Further Investigation of AGFA Filmfabrick (Photographic Plant), Wolfen, Near Léipzig* (C22/ 1871; S.O. Code No. 51-3275.55), found during the visit to the Gevaert archive. The gathered information here suggests that CTA commercial production might have started in 1930 in Germany and Belgium.

Regarding CAB production, when compared with western companies, Gevaerts started the production of CAB base later and kept it for a short period of time (Tables 2.2 and 2.4). By considering the reports on CAB base stability, it is not clear why Gevaert produced this polymer for only two years.

Moreover, based on the information given by Mr. Van Leemput, it is reasonable to suggest that from 1910 until 1930 Gevaert was in a stage of research and development of technology in order to accomplish the manufacturing conditions to implement the commercial exploitation of cellulose esters, quoting:

> *A group of (French) researchers had little success to increase production and improve quality. After two serious fires (1922 and 1923), the researchers were replaced by dr-is. Aladar Schuller (Hungarian). In 1926 successfully, cellulose nitrate could be cast on an endless copper band. In 1928 in Heultje (Westerlo: rural areas for the sake of fire risk), a raw materials plant for cellulose nitrate was built. In 1930 the research and the production of cellulose nitrate and diacetate were entrusted to a group of highly qualified specialists under the leadership of A. Schuller. In 1933 the development of triacetate was added to this group.*

This information may support the different degradation pathways and a lifetime of plastic negatives with cellulose ester base as it shows that the industry of photography was relying on the quality of CN stocks from other producers and therefore did not control the production process.
These facts do not support the overall history of development and production of film-based negatives in Europe (or any place else); however, it gives some clues about the commercial and industrial processes that were carried out at that time. Furthermore, it also gives insightful information about how the photography industry supplied their needs to produce film-based negatives for the markets. In the same manner, the information presented in Tables 2.2 and 2.4 shows a gap in the production's chronology of the aforementioned companies. This data does not represent the broad manufacture of cellulose esters films by other producers; however, it launches a perspective on the timeline of production of plastic negatives with cellulose esters.
Thus, considering the vast experimentalism that characterizes this period, it is important to know the materials and their production to better enable the prediction of their degradation process.

2.2 Cellulose ester film-based negatives: understanding the composition and manufacture

As generically described above, cellulose esters or cellulose derivatives are obtained by chemically treating natural polymers such as cellulose with a mixture of acids. In the esterification reaction that results in cellulose esters, the hydroxyl groups (-OH) in cellulose are replaced by nucleophilic groups. The reaction is carried out in the presence of mineral acids or organic acids (or their anhydrides) and a catalyst (Balser et al. 2012, 333,335).
Despite the strong intermolecular forces in cellulose (40 kJ energy per mole of repeating unit), the hydrogen bonds are decreased when the OH groups are replaced by ester groups (or acid anions) and consequently result in more soluble and less crystalline polymers, such as cellulose derivatives (Hamrang 1994, 2).
The esterification process may occur by full or partially replacing OH groups with (x) nitro or acetyl groups substituents, which can be shown as:

$$H - [C_6H_7O_2\ (OH)_{3-y}\ (O_x)]\ z\ OH$$

The degree of substitution (DS) is represented by (y) and the degree of polymerization (DP) by (z). The properties of cellulose derivatives rely on the type and degree of substitution performed. Two routes are proposed to define the degree of polymerisation, one is by the average number of substituent groups per unit, ranging from 0 to 3, and the other option is by the mass percentage of the nitro or acetyl groups present, which can range from 0% to above 50% (Hamrang 1994, 3).

With this description it was intended to introduce the chemical reaction through which CN and CA polymers are obtained. Nevertheless, given the topic of this research, in the following sections of this chapter in-depth information about CN and CA films composition and manufacture will be presented to support the results and discussions in the chapters ahead.
Since this study is focused on the chemical behaviour and decay of cellulose esters film-based negatives, it was considered important to gather the disperse information related with the raw material (cellulose) used to produce those films, as well as information about the manufacturing conditions used.
This topic will be further introduced in Chapter 4, where the results obtained in the identification and assessment of the selected film collections for this study are discussed.

2.2.1. Raw material: cellulose

Cellulose is a natural polymer, a polysaccharide composed of f β(1→4) linked D-glucose units $(C_6H_{10}O_5)_n$ existing as a fibrous form in the structure tissue of the cell walls of plants such as cotton and wood (Hamrang 1994, 1; Stewart 1997, 5; Sirkis 1982, 5). In Fig. 2.3 the chemical structure of cellulose is shown.

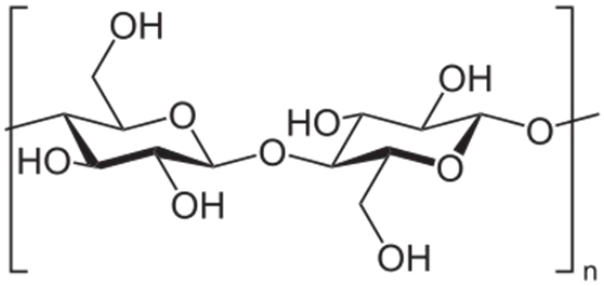


Figure 2.3 – Chemical structure of cellulose

The cellulose content varies according to their original source. Thus cellulose average content of wood fibres ranges from 40% to 50%, while for flax and sisal is about 75%, and cotton have the highest cellulose content of 94% (Wypych 2016a). Therefore cellulose obtained from cotton fibres is considered the purest (Wypych 2016a).
The homogeneity of the esterification reaction and the viscosity of the final product rely on the chemical composition of cellulose (DP and polydispersibility) and the fibers morphology (fiber length and distribution, cross-section form and thickness of the secondary wall, and packaging, degree of crystallization and arrangement of the fibrils) (Balser et al. 2012, 339).
Furthermore, the rate, type and distribution of hemicellulose and lignin in the cellulose structure are also decisive for the esterification reaction (Balser et al. 2012).
The high degree of intermolecular and intramolecular OH bonding (dipole-dipole interaction) between the hydroxyl groups present in cellulose molecule establish the

polymer high crystallinity, stiffness, solubility (or insolubility in water) and its low internal flexibility (Hamrang 1994, 2; Sirkis 1982, 6).

The percentage of crystalline and amorphous states change according to the sources of cellulose. By comparing the crystalline state of cellulose extracted from wood fibres and cotton, it was found that the former has lower values of crystallinity (50-70%) and the latter has a higher percentage (95%) (Biermann 1996, 32–33). Additionally, the degree of polymerization (DP) varies according to the type of cellulose source, being found that the DP of cotton ranges between 800 and 10.000 repeating units while wood has the lowest DP ranging between 300 and 1700 repeating units (Wypych 2016a).

The high quality and purity of cellulose obtained from cotton made it the major raw source for producing cellulose esters (Saka 2004a, 29; Worden 1916a, 2503; Barsha 1954, 715), followed by wood pulps (Saka and Matsumura 2004, 37).

The selection of the raw material relied on the chemical composition of cotton and wood fibres. Cotton cell walls are mainly composed of cellulose while wood is rather a composite of cellulose, hemicellulose and lignin (Saka and Matsumura 2004, 37; Saka 2004b, 9,13). In order to be used in the production of cellulose esters, wood fibres must be pulped and bleached to remove lignin and hemicellulose, and consequently improve the quality and purity of the cellulose extracted (Saka and Matsumura 2004, 37; Barsha 1954, 715).

In the framework of this study, it was questioned if there were enough supply of cotton to produce cellulose esters at the beginning of the 20th century, especially considering the WWI period. The review of literature confirmed that the industry faced a scarcity of cotton and started to use other sources of cellulose (Barsha 1954, 716; Balser et al. 2012, 339). One confirmation came from J. Barsha[33] (1954, 716) who wrote that:

> *During World War I, large quantities of wood pulp (usually in the form of crepe tissue paper) were nitrated in Germany. During the same period of scarcity of cotton, the nitrocellulose industry in the United States* (of America) *changed first from millrun linters to second cut linters and later to hull fibre.*

Barsha (1954, 716) describes that to increase the internal supply of raw materials, in the 1910's North Americans and Germans searched for new methods to perform large-scale nitration of crepe paper. Nevertheless, it was found that the nitration process with crepe paper was difficult, and in the early 1920's further research to develop methods for purification of wood pulps were carried out (Barsha 1954, 716). Two methods were used to purify cellulose extracted from wood pulps, the sulphite and the sulphate processes (Saunders and Taylor 1990, 169). In the former process, a solution of calcium bisulfite ($Ca(HSO_3)_2$) was used while in the latter, a mixture of sodium hydroxide (NaOH), sodium sulphide (Na_2S) and sodium carbonate (Na_2CO_3) (65:15:20) was used. The cellulose obtained with the sulphite process has an α-cellulose content ranging from 92-95%,

[33] Assistant to Manager, at the Hercules Powder Company, Wilmington, Delaware. U.S.A.

while cellulose obtained with the sulphate process has a 96% α-cellulose content (Balser et al. 2012, 339). Furthermore, the acid retention capability also changes according to the cellulose source. It should be pointed out that cotton linters have the lowest acid retention capability (110-130%) compared with purified wood pulps which show higher values (230% for sulphate pulps and 300% for sulphite pulps) (Balser et al. 2012, 339).
In sum, despite the known advantages of cotton linters, this material has not always been the raw source to produce CN and CA polymers. New options were searched for due to financial restraints and scarcity of cotton linters. Wood pulp and crepe paper were found to be used for this purpose in the literature. The selected literature also shows that the technological improvements in pulping techniques allowed to obtain a purified cellulose (95% α-cellulose content) by removing hemicellulose and lignin and favoured the production of CN and CA, as well as promoting a reduction in production costs (Balser et al. 2012, 339,355). Nevertheless, according to the literature, wood pulp lacks the high quality of cotton linters.

2.2.1.1 - Remarks on the use of wood pulps for production of cellulose esters

As presented above, wood pulps were used as cellulose sources for production of cellulose esters. In the framework of this investigation, the drawbacks related to the use of wood pulp for esterification were found to be relevant. Notes on the quality of CN and CA produced with wood pulp are given since these may support the discussion of the results achieved in this work.
According to Julie A. Reilly[34]

> *The inherent qualities of the original cellulose are partially retained by the finished celluloid. For this reason, one potential source of deterioration in cellulose comes from the instability of the cellulose molecule and the chemicals used to process the cellulose.* (Reilly 1991, 147)

The rate and homogeneity of the diffusion of the nitration mixture in the cellulose structure dictates the final properties of CN obtained (Saunders and Taylor 1990, 170; Short 1986, 3). Thus, and regarding the use of wood pulp to produce CN, initially, it was found that the fibres […] *swelled considerably during nitration and retained more acid than the nitrocellulose made with cotton*. […] (Saunders and Taylor 1990, 169). Also, the properties of CN were affected by the type of purification process used for improving the quality of wood pulps (Saunders and Taylor 1990, 170). According to the literature, CN produced with sulphite fibres has a variable DP and high molecular weight

[34] Executive Director of the Intermuseum Conservation Association (ICA) Art Conservation, at Cleveland, United States of America. Reilly authored an extensive work on CN and CN applications for production of a variety of objects.

comparatively with CN produced with sulphate pulps and cotton (Strecker and Trucker, 1980, as cited in Saunders and Taylor 1990, 170). This is a contradictory perspective if the properties of cotton linters and wood pulps given above were considered. However, it is important to emphasize that Strecker and Trucker conclusions were supported by nitration tests in which different cellulose sources were used and through which it was found that the molecular weight distribution also contributes to the nitration reaction and properties of the final product (Strecker and Trucker, 1980, as cited in Saunders and Taylor 1990, 170).

Wood pulps were also used to produce CA, again mostly due to the scarcity of cotton and also because of the costs associated with the production of cotton linters (Ballany 2000, 8). Initially, wood pulps were commonly used for producing lower-quality products (Balser et al. 2012, 355). Therefore, the final products manufactured with wood pulps show […] *poor colour and clarity* […] (Ballany 2000, 8). Considered to be unsuitable for the manufacture of transparent film supports, improved purification procedures were implemented to overcome drawbacks caused by extreme conditions used in the aforementioned purification methods.

Based on this information, it is possible to propose that cellulose ester film-based negatives produced during WWI by the esterification reactions of wood pulp may have been chemically more unstable.

2.2.2. Cellulose nitrate

Cellulose nitrate is obtained by replacing the hydroxyl (-OH) groups on cellulose by the NO_2 group (Fig. 2.4). The properties of CN polymer, also known as *inorganic ester,* vary according to the degree of nitration, thus determining the different possible applications (e.g. propellant, film or coating).

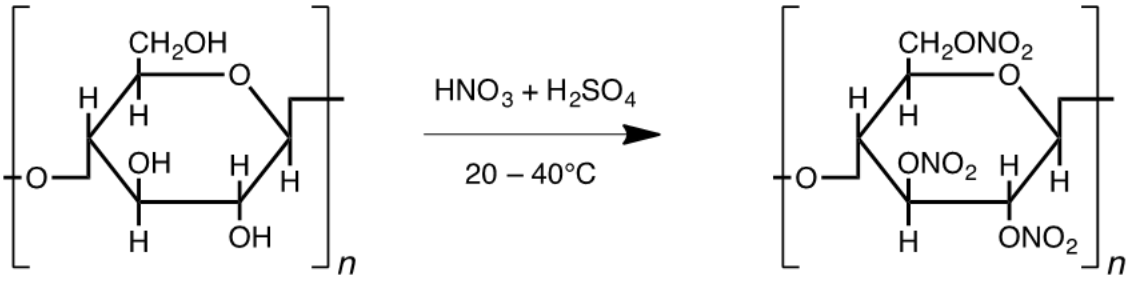


Figure 2.4 – Esterification of cellulose to cellulose nitrate with reference to the mixed acids solution, and temperature conditions (as in Shashoua 2008b, 41).

Cellulose nitrate $[C_6H_7(NO_2)_3O_5]_n$[35] is prepared through an esterification (nitration) process taken under an interval of temperature ranging between 35 to 40ºC during 20 to 60 minutes (Hamrang 1994, 6). The nitration procedure is performed in a continuous

[35] Cellulose nitrate is a misnomer once it contains C-O-N bonds rather than C-N bonds, which are characteristic of nitro compounds (Shashoua 2008a, 40; Reilly 1991, 147).

and automatic process in which dried cellulose is chemically treated with a mixture of nitric acid, sulphuric acid (condensation agent) and water at 25, 55, and 20% respectively (Selwitz 1988, 11; Hamrang 1994, 6; Stewart 1997, 7) (Figs 2.4 and 2.5). The use of sulfuric acid (H_2SO_4) showed to benefit the esterification reaction since it acts as a catalyst and allows the reaction to take place under standard room conditions.

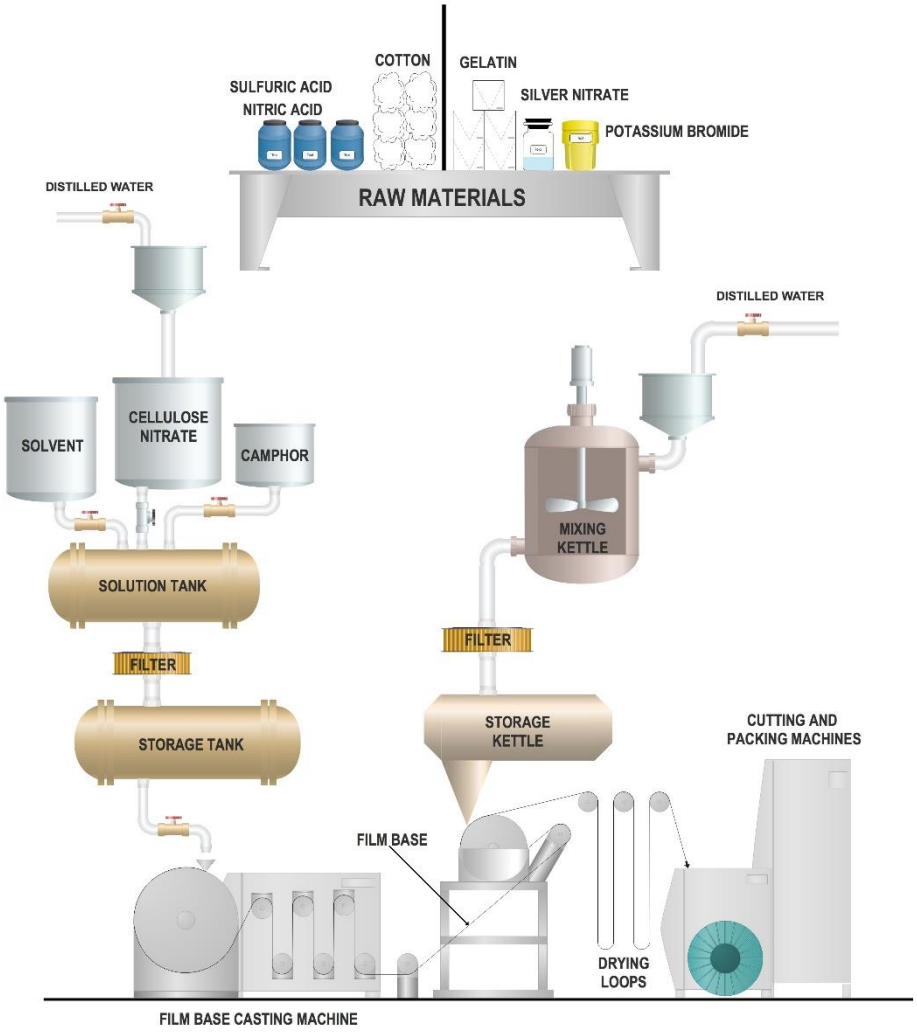


Figure 2.5 – Flow diagram of CN and CN film-based negatives production. ©Élia Roldão/Credit Daniel Cristo.

Broadly, four production steps are performed to obtain CN, which are: nitration, purification, digestion and dehydration (Selwitz 1988, 11) (Fig. 2.5.). The final production steps were preventive steps through which the detrimental effect of water and acids used in the production were removed and therefore, the stability of the material was improved (Selwitz 1988, 11). Besides these production steps, in order to obtain a clear polymer, bleaching with sodium hypochlorite (NaClO) was performed (Hamrang 1994, 6).
In the course of the reaction, hydroxyl groups (-OH) on the C2, C3 and C6 positions of the cellulose molecule are replaced by nitrate groups $(ONO_2)^-$ (Fernández de la Ossa et

al. 2011, 1740; Stewart 1997, 7; Sirkis 1982, 6) (Fig. 2.4). The replacement depends on the reactivity and position of each -OH gr in the cellulose molecule (Shashoua 2008a, 41). Table 2.5 was designed in the framework of this study and summarises CN's nitrogen contents and applications according to different DS.

Table 2.5 – Summary of cellulose nitrate's with different DS and respective nitrogen content (%) and applications (Brydson 1999, 616; Fernández de la Ossa et al. 2011, 1741; Stewart 1997, 7; Sirkis 1982, 7; Shashoua 2008a, 41)

DS	Nitrogen content (%)	Applications
Mononitrate	6.76%	_____
Dinitrate	11.11	
	10.7-11.1	Plastics, lacquers
	11.2-12.3	**Films, lacquers**
	12.4-13.5	Explosives, cordite
Trinitrate	14.14	_____

In theory, the -OH gr in the C6 position (primary alcohol) is the first to be esterified, followed by the -OH grs in C2 and C3 positions (secondary alcohols), respectively (Stewart 1997, 7; Sirkis 1982, 6; Selwitz 1988, 11). According to the data presented in Table 2.5, films are produced with dinitrates with nitrogen content ranging between 11.2 and 12.3% and DS between 1.9 to 2.7 -OH grs (Sirkis 1982, 6–7; Shashoua 2008a, 41). Regarding the distribution of NO_2 grs, it is believed that CN with a DS of 2.3 (nitrogen content= 12.2%) […] *contains 50% trinitrated rings, 34% dinitrated rings and 16% mononitrated rings and essentially no rings without nitrate esters* […] (Selwitz 1988, 9). Fig. 2.5 presents a diagram of the production of CN polymer and photographic film. According to C. B. Neblette, two methods were used to obtain a CN viscous dope which consisted of the evaporation of solvents from the dope or in *coagulation with a non-solvent* (Neblette 1952c, 151). As described by Neblette, by dissolving CN with 11 to 12.4% nitrogen in a mixture of solvents (e.g. acetone with methyl or ethyl alcohol, or less frequently with butyl alcohol) a CN's dope was obtained (Neblette 1952c, 151). Subsequently, plasticizers (see section 2.2.2.1) were added to the dope and a filtration was performed to retain impurities. The dope was then poured on the wheels or cylinders and afterwards they were coated with a photographic emulsion (see section 2.3).

2.2.2.1 - Plasticizers

Besides the references and description of plasticizers, in the framework of this study, it was not found literature that mentioned other additives (e.g. anti-oxidants and UV stabilizers) used to improve CN film-based negatives properties. Therefore, it will only be presented the range of plasticizers used to improve the properties of cellulose esters film-based negatives.

Brittleness and stiffness limited CN's utilization. In part, these disadvantages resulted from CN's fibrous nature retained from cellulose (Stewart 1997, 7). These drawbacks were overcome by adding plasticizers to CN dope improving its flexibility and workability (Stewart 1997, 7). Additionally, by adding plasticizers the glass transition temperature and the polymer's modulus of elasticity are decreased (Stewart 1997, 7). Furthermore, the plasticization conditions and type of plasticizer dictate the success of the polymer-plasticizer system.

A broad type of plasticizers namely oils (castor oil, vegetable oils, fatty oils), nitrobenzole and camphor were used to improve CN's properties (Böckmann 1907, 1; Shashoua 2008a, 41). From the set of plasticizers, camphor was the first commercially successful plasticizer used in CN.

Camphor is a resin extracted from *cinnamum camphora* tree existing in Asia and Florida (J. A. Reilly 1991, 149). It belongs to the terpenoid family and has a primary structure 1,7,7 – trimethylbicyclo (2,2,1) hepta-2-one that sublimes at room temperature (Reilly 1991, 149; Selwitz 1988, 46) (Fig. 2.6).

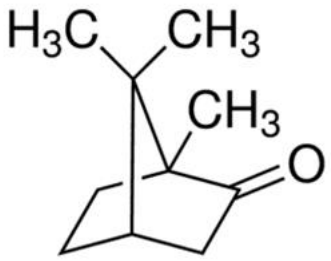


Figure 2.6 - Chemical structure of camphor

Overtime the contribution of camphor was understood, it was found that by adding larger amounts of camphor to CN (30-25 % to 70-75% respectively) it was possible to improve CN properties (Sirkis 1982, 7; Balser et al. 2012, 349). From this CN-camphor system, a final product known as *Celluloid* was produced (Shashoua 2008a, 41; Saunders and Taylor 1990, 161). Despite its success, the CN-camphor system is not clear. According to the literature, two hypotheses were postulated for the successes of CN-camphor system. One suggests that the complex is based on the bonding *between the carbonyl group of the camphor molecule* with the non-substituted hydroxyl group present in the cellulose dinitrate (Yarsley and Flavel et. al, 1964, as cited in Sirkis 1982, 8). The second was postulated by F. D. Miles who concluded that the carbonyl (ketone) group in camphor is linked to the nitrate groups (Miles, 1955, as cited in Sirkis 1982, 8). Miles supports his theory on the fact that by increasing the nitrogen content, a higher absorption of camphor is detected (Miles, 1955, as cited in Sirkis 1982, 8).

After WWI the replacement of camphor was tested. Initially, synthesized camphor[36] was used for industrial production of CN products, however, despite the similar

[36] Synthetized camphor was obtained by *converting α-pinene from turpentine to camphene, next converted to isobornyl acetate, which is converted to isoborneol next transformed to camphor* (Reilly 1991, 149).

characteristics, none of the synthesized camphor was able to replace the natural product (Reilly 1991, 149). According to Julie A. Reilly, a mixture of both types of camphor (natural and synthetized) may have been used (1991, 149).

Besides camphor, other plasticizers such as tricresyl phosphate (TCP) ($C_{21}H_{21}O_4P$) and triphenyl phosphate (TPP) ($C_{18}H_{15}O_4P$) have been used (Reilly 1991, 149; Saunders and Taylor 1990, 161; Stewart 1997, 8). Due to its flame-retardant nature, TPP was the first to be used in replacing camphor.

Moreover, Pierre Glafkidés[37] indicates the use of a mixture of camphor and plasticizers from the phthalate and phosphate family, designated as *Schleussner formulation,* to plasticize CN polymer (Table 2.6) (1949, 275–93).

Table 2.6 - Products applied in the *Schleussner* formulation used to plasticize cellulose nitrate (Glafkidès 1949)

Products	Quantity
Cellulose nitrate	250 parts
Acetone	900 parts
Camphor	38 parts
Tricresylphosphate	0.5 parts
Phthalic ester	1 part
Butylic alcohol	25 parts
Ethylic alcohol	135 parts

The use of tricresylphosphate (plasticizer and fire retardant) is associated to the production of CN lacquers (Glafkidès 1949; Saunders and Taylor 1990, 161), being used since 1910 to partial replace camphor (Shashoua 2008a, 61–62). Later, before WWII camphor was replaced by plasticizers from the phthalic and phthalate families, e.g. tryphenil and trycresil phosphates, and dibutyl and di(ethylhexyl phthalate) (Shashoua 2008a, 177).

Furthermore, specific reference to the use of Palatinol A[38], also known as diethyl phthalate was found in the *British Intelligent Objectives Sub-Committee Report Further Investigation of AGFA Filmfabrick (Photographic Plant), Wolfen, Near Léipzig* (C22/ 1871; S.O. Code No. 51-3275.55). According to this report, in 1946 Palatinol A and camphor were added to CN bases, which were produced at the Deutsche Celluloid Fabrick[39], in Eilenburg, Germany.

[37] Pierre Glafkidès (1912 -).

[38] Diethyl phthalate (phthalic acid diethyl ester) acts as a light stable, fast-fusing plasticizer (phthalate) in cellulose acetate and cellulose nitrate.

[39] One of Gevaert cellulose nitrate suppliers.

2.2.3. Cellulose acetates: The Safety option

As previously described, the designation of CA encompasses CDA, CTA, CAB and CAP polymers. Thus, comparatively with the sections where CN polymer and CN film-based negatives are described, the sections that focus on CA's polymer and CA's film-based negatives are broader since they cover a wide range of information.

In the 1920's, CA film-based negatives started to be commercially available in the markets and gradually replaced CN film-based negatives. To distinguish both, the designation 'Safety films' was given to CA film-based negatives indicating their non-flammable nature.

CA is obtained through an esterification reaction in which the -OH groups present in cellulose molecule are replaced by acetyl groups (-$OCOCH_3$) (Shashoua 2008a, 41).

Fig. 2.7 illustrates the acetylation reaction necessary for obtaining a primary acetate (CTA), in which a full acetylation of the cellulose molecule (replacement of the primary and secondary -OH grs) occurs (Balser et al. 2012, 354). The hydrolysis reaction of CTA to obtain a secondary acetate (CDA) is also shown in Fig. 2.7.

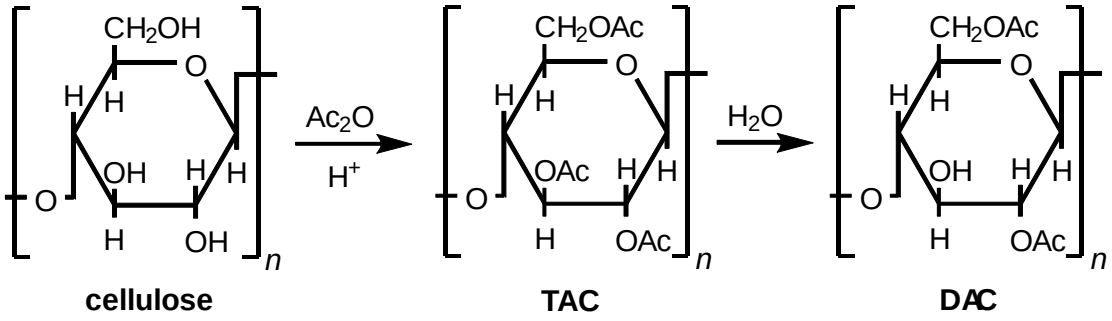


Figure 2.7 - Esterification of cellulose to cellulose triacetate and cellulose diacetate (Hamrang 1994, 12).

At the beginning of the 20th century, CTA had no commercial significance due to its specific solubility on chlorinated solvents, which at the time were expensive (Shashoua 2008a, 41). In 1906, G. W. Miles[40] discovered and patented a method through which CTA was hydrolyzed with sulphuric acid and CDA was obtained (Purves 1954, 38). Soluble in common and cheaper solvents such as acetone, CDA became a commercial success (Shashoua 2008a, 42; Ballany 2000, 4) (Fig. 2.7).

Regarding CA's polymer production, the acetylation process involves several steps. In practice, the production process starts with a pre-treatment of cellulose followed by esterification, hydrolysis, filtration, precipitation, washing, dehydration, centrifuge and screening processes (Malm and Hiatt 1954, 775–81; Hamrang 1994, 9–11).

[40] American chemist who discovered and patented the first method to perform the partial hydrolysis of cellulose acetate (U. S. Patente 838, 350).

Figure 2.8 is a historical illustration of CA photographic materials production from Gevaert found during the visit to Agfa-Gevaert archive carried out in the framework of this study.

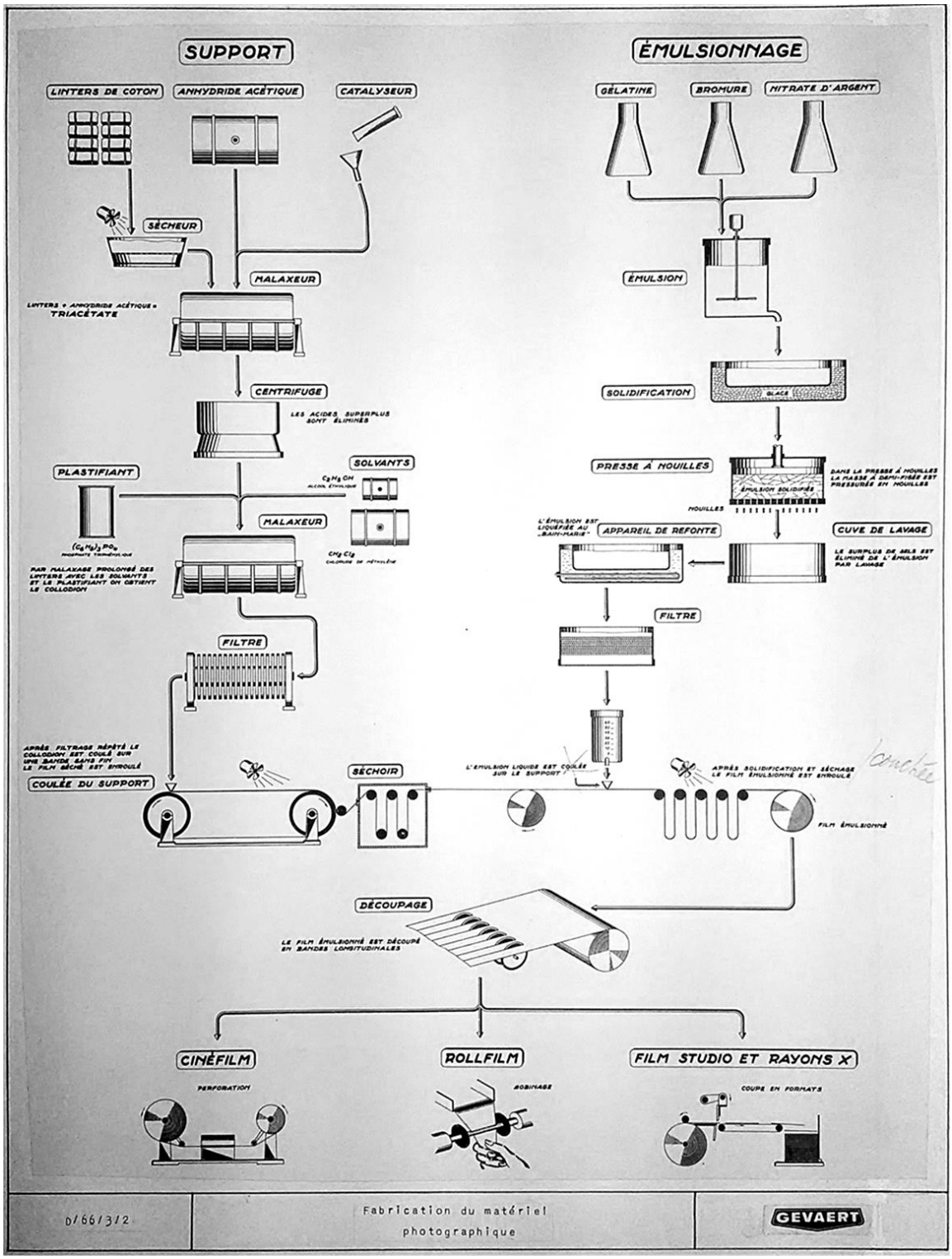


Figure 2.8 – Cellulose acetate film-based negatives production: film base (left) and photographic emulsion (right). © Agfa-Gevaert Archive.

In this document, it is possible to understand CA's production process performed by Gevaert.

The uniformity, efficiency and speed of the acetylation reaction relied not only on the manufacturing steps but also, as previously said, on the raw material (Hamrang 1994, 9). Cellulose morphology is challenging (Balser et al. 2012, 356). Aware of this fact, in the early 1900's, a pre-treatment (or activation treatment) of cellulose molecule was introduced by Bayer and Co. In performing this treatment, the state of aggregation of the cellulose molecule was changed, therefore making it a more reactive and homogeneous esterification reaction (Krässig et al. 2012, 356; Hamrang 1994, 12; Ott et al. 1954, 31). In sum, the hydroxyl grs in the cellulose molecule becomes more available thus allowing the solvents to diffuse in the acetylation reaction (Balser et al. 2012, 356). In practice, in the pre-treatment step the cellulose fibres are swelled through the action of swelling agents (e.g. water, alcohols, acetic acid, amines, aliphatic acids and aqueous sodium hydroxide) (Worden 1916b, 583–650; Balser et al. 2012, 356). The pre-treatment conditions (acetic acid ratio, temperature and activation times) varied according to the producers (Balser et al. 2012, 356).

The pre-treatment efficiency could be improved by adding sulfuric acid to the activation medium (Krässig et al. 2012, 356; Hamrang 1994, 9; Ballany 2000, 6). This way, the reaction improves by extending the time necessary to distribute the catalyst, reduce the fibre length (hydrolysis) and achieving a homogeneous swelling of the fibres (Balser et al. 2012, 356). Additionally, by using sulphuric acid in the pre-treatment solution it was performed a slight acetylation at low exothermic conditions (temperatures < 50ºC) (Hamrang 1994, 9; Ballany 2000, 6).

The presence of moisture within cellulose (4-7%) is beneficial for the activation step. The moisture content depends on the drying methods used by each producer (Balser et al. 2012, 356).

The second step for cellulose acetate production involves the esterification process or acetylation in which two significant industrial methods are used: the heterogeneous system or non-solvent process and the acetylation in a homogeneous system or solvent process (Hamrang 1994, 10; Balser et al. 2012, 355,357).

In the heterogeneous process, cellulose is acetylated with non-polar solvents such as carbon tetrachloride (CCl_4), benzene (C_6H_6) or toluene (C_7H_8) (Balser et al. 2012, 357–58). The rate of the reaction relies on the presence of a catalyst and on temperature (c. 50ºC) (Ballany 2000, 8; Krässig et al. 2012, 357–58). In this process perchloric acid ($HClO_4$) is the catalyst preferred, in detriment of sulphuric acid (Balser et al. 2012, 357). From this process results a 'fibrous acetate' (the fibre structure of cellulose was kept) impossible to hydrolyse. Thus, comparatively with the homogeneous process, the use of 'fibrous acetate' is limited (Balser et al. 2012, 358).

Concerning the solvent or the homogeneous process, two processes can be performed: the 'acetic acid process' and the 'methylene chloride or Dormagen process' (Hamrang 1994; Balser et al. 2012, 355,357).

In both options, the reaction starts as a heterogeneous system. In the course of the reaction, the cellulose fibres dispersed in the reactants are dissolved and a homogeneous and highly viscous solution of CTA is obtained (Hamrang 1994, 10; Balser et al. 2012, 356). From the several acetylation reagents used (e.g. acetic acid (CH_3COOH), acetyl chloride (CH_3COCl)), glacial acetic acid (CH_3COOH), acetic anhydride ($C_4H_6O_3$) (10-40%), and sulphuric acid (2-15%) are regarded as the most successfully used in the 'acetic acid process' (Ballany 2000, 8; Krässig et al. 2012, 357). As mentioned previously for the pre-treatment step, the amounts of the reactants used in acetylation rely on the producer's options (Balser et al. 2012, 357). The selection of these solvents also rely on the advantage of being easily recovered and reused (Ballany 2000, 8). The reaction is temperature dependent and it usually is performed at temperatures up to 50ºC (Balser et al. 2012, 357).

Additionally, there is also the possibility to get the homogeneous process to produce CTA by performing an esterification reaction with methylene chloride (CH_2Cl_2). Designated as methylene chloride or Dormagen process, this process became known for […] *the only practical solvent for commercial use* […] (Williamson 1994, 6). As previously said, the Dormagen process may have been carried out prior to WWII.

The Dormagen process consists on acetylation of pre-treated cellulose with a mixture of acetic anhydride, sulphuric acid and methylene chloride (300:1:400, respectively) (Hamrang 1994, 11; Williamson 1994, 11). Due to the excellent solubility of CTA in methylene chloride, only a low concentration of sulphuric acid (1%) was necessary to catalyse the reaction (Balser et al. 2012, 357). Furthermore, methylene chloride's low boiling point (*bp* 41º) allows for a better control of the reaction's temperature (Balser et al. 2012, 357).

From the homogeneous acetylation processes, a primary cellulose acetate (CTA) is produced which after it is hydrolysed to obtain a secondary cellulose acetate (CDA) (Williamson 1994, 11; Hamrang 1994, 11).

Two methods were used for the CTA hydrolysis (Malm and Hiatt 1954, 778–80; Williamson 1994, 11):

i) a mixture of water and acetic acid is used to prevent precipitation of the polymer, removing residues of acetic anhydride and simultaneously keeping the viscosity of the solution.

ii) to the former method (a) sulphuric acid was added at elevated temperatures allowing the rate of the hydrolysis reaction to accelerate. After complete hydrolysis the reaction was interrupted by adding magnesium (Mg), sodium (Na) or calcium acetate ($C_4H_6O_4Ca$) and a chloride salt (Hamrang 1994, 11; Ballany 2000, 9; Krässig et al. 2012, 359).

After reaching a CA with the desired DS, the polymer is precipitated, followed by centrifugation and washing (Ballany 2000, 9). Residues of hydrogen sulphate esters

groups were removed from the dope by boiling it in diluted sulphuric acid (0.02% for 2 hours) and washing it in cold water (Hamrang 1994, 12; Ballany 2000, 10). To reinforce the stability, the polymer was dried thus reducing the moisture content up to 2% (Hamrang 1994, 12).

Besides CA, cellulose mixed esters of acetic and propionic acid[41] (cellulose acetate propionate -CAP) and acetic and butyric acid[42] (cellulose acetate butyrate-CAB) were also produced. These polymers were manufactured according to the homogeneous solution process described above, however, the esterification solvents were different (Balser et al. 2012, 363). CAP was used as support for amateur movie films (Adelstein 2010, 389) thus its chemical structure or degradation will not be discussed here since the focus is still film negatives. Thus, from this point on only the CAB polymer be and the CAB film-based negatives are discussed.

Two methods could be performed to manufacture CAB:

i) by esterifying pre-treated cellulose with a mixture of butyric acid, acetic anhydride, and 0.5% sulfuric acid (catalyst) (Hamrang 1994, 16) or,

ii) by performing a pre-treatment of cellulose with the solution presented on a) where a small amount of water and butyric acid is added (Essel and Mork process) (Malm and Hiatt 1954, 786).

CAB with different DS was obtained by hydrolysing cellulose tributyrate (Malm and Hiatt 1954, 786). Two methods are pointed out for the hydrolysis of the CAB: the Gault and Angla method and the Herzog and Frank method (Malm and Hiatt 1954, 786).

In the Gault and Angla method, a straightforward hydrolysis of c*ellulose tributyrate* is performed with butyric acid, at temperatures ranging from 45º to 50º C.

Unlike the aforementioned process, in the Herzog and Frank method the hydrolysis starts with the treatment of cellulose with formic acid (87%) at 20ºC, followed by washing and drying to finally perform the esterification step with a mixture of butyric anhydride and butyric acid with zinc chloride (catalyst) (Malm and Hiatt 1954). In the end, the final product obtained is hydrolysed in 95% butyric acid at 90ºC, for 32 hours.

The control of the manufacturing process was decisive for the properties of the polymer. CA polymer is characterized by its molecular weight (MW), the degree of polymerization (DP) and degree of substitution (DS). DS determines the physical properties and the supramolecular structure. Therefore, according to the number of acetyl groups in the anhydroglucose unit, it is obtained a mono, di or tri substituted cellulose, corresponding to a DS 1 to 3. Table 2.7 summarises the DP, acetic acid yield, acetyl content and solubility according to CA's DS. Additionally, Table 2.7 also shows the variety of products produced

[41] Chemical formula of propionic acid: $C_3H_6O_2$.

[42] Chemical formula of butyric acid: $C_4H_8O_2$.

with CA according to the DS, being highlighted those which were used as film supports (bold).

Table 2.7 – Summary of commercial cellulose acetate DS, acetic acid yield, acetyl content (%), average DP, solubilities and applications (Williamson 1994, 6; Brydson 1999, 623)

DS	Acetic acid yield (%)	Acetyl content (% - $COCH_3$)	Av. DP	Solubility	Applications
2.2 - 2.3	52.1 - 54.3	37.6 - 38.7	200-250	Soluble in acetone	Injection moulding
2.3 - 2.4	**54.3 - 56.4**	**38.7 - 40.1**	**250-300**	**Soluble in acetone**	**Film**
2.4 - 2.6	56.4 - 59.3	40.1 - 41.6	---	Soluble in acetone	Lacquers
2.9 - 3.0	**60.7 - 62.85**	**43.7 - 44.8**	**---**	**Soluble in chloroform**	**Triacetate film** and fibre

Commonly, an incorrect attribution of DS 3 is given to CTA which in practice has a value of 2.8 to 2.9, while CDA has a DS ranging between 2.2 to 2.5 (Ballany 2000, 8).
Regarding the structure of CA polymer, the distribution of the acetyl groups will influence the structure of the polymer. Theoretically, the acetylation occurs randomly in the C_2, C_3 (secondary) and C_6 (primary) positions of the anhydroglucose unit. However, due to the reactivity nature of C_6 and C_2 positions (which are more exposed), it is proposed that those are the first to be esterified (Derham et al. 1992, 135).
The macromolecular structure of the CA is similar to the cellulose structure, having a helical symmetry. However, the dimensions of the acetyl group and the crowding effect found between groups lead to the formation of a […] *more opened helical coil*. (Derham et al. 1992, 135). The helical symmetry becomes more compacted with the increasing of the polymer DS (Fig. 2.9) (Derham et al. 1992, 136).

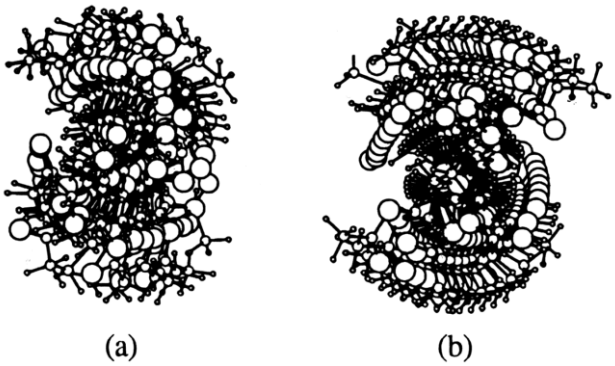


Figure 2.9 – Illustration of the quaternary structure of CA partially esterified (a) and fully esterified (b)(adapted from Derham et al. 1992, 136).

The presence of areas with micro-crystallinity allows us to state that CA is a semi-crystalline polymer, however, CDA is less crystalline than CTA (Balser et al. 2012, 361).

These areas act as junction points of the polymer network and influence the mechanical properties of the polymer, therefore, in part, support the different physical properties between CDA and CTA. A summary of cellulose CA and CAB properties is presented in Table 2.8.

Table 2.8 – Summary of properties of cellulose, cellulose acetate and mixed esters (CAB) polymers (adapted from Malm and Hiatt 1954, 791)

		Behaviour on heating			% Moisture regain					
Polymer	**C** atoms**	**Shrinking point (ºC)**	**Melting point (ºC)**	**Water tolerance value**	**RH 25 (%)**	**RH 50 (%)**	**RH 75 (%)**	**RH 95 (%)**	**Density (g/mL)**	**Tensile strength (kg/m m^2)**
Cellulose*	0	-	-	-	5.4	10.8	15.5	30.5	1.52	-
Acetate	2	-	306	54.4	0.6	2.0	3.8	7.8	1.28	7.3
Butyrate	4	178	183	16.1	0.1	0.2	0.7	1.0	1.17	3.1

*Deacetylated cellulose with 40.4% acetyl content; ** C atoms in the substituents of OH.

Furthermore, CA polymer with lower DS tends to be less resistant to moisture or, in other words, it is more hygroscopic due to the availability of existing OH grs reacting with water molecules (Table 2.8) (Edge et al. 1988). Chemically CAB is different from CA, the former is mostly highlighted for low moisture absorption (Hamrang 1994, 17) (Table 2.8.) This is an important property considering the stability of the polymer.
The plasticizers compatibility and solubility in polar solvents increases for CA polymers with lower DS, and the reverse situation is highlighted for CA with higher DS (Balser et al. 2012, 360). Again, the DS of the polymer is also important when considering the stability and lifespan of film-based negatives. These chemical properties are important in the discussion of the results in this study (see Chapter 6).

2.2.3.1. Contributions to the historical framework of the production CA film-based negative

Regarding the manufacture of CA film supports, the film is obtained by mixing cellulose acetate (flake) with a mixture of dichloromethane and methanol to obtain a dope, later adding a plasticizer (Hamrang 1994, 13; Williamson 1994, 14) (Fig. 2.8).
Regarding the dissolution of 'dope' (a highly viscous mixture), according to the type of CA polymer used for the production of the base for still negatives, different solvents were pointed out (Neblette 1952c, 152). As expected the dissolution of the acetate dope (CA with 38 to 40% acetyl content) was performed in acetone or also with phthalates, which also had a solvent action in the processing of CDA (Malm and Hiatt 1954, 840–45).
Concerning CAB, the dope was dissolved in a mixture of chlorinated hydrocarbons (e.g. ethylene or propylene chloride) with methyl or ethyl alcohol, while CTA flakes were dissolved on a mixture of methylene chloride and alcohol solution (Neblette 1952c, 152).

The 'dope' obtained was filtered (Hamrang 1994, 13) and ran in chromium or stainless steel drums or belts. This action was performed in sealed chambers, in which by applying hot air the solvents were forced to evaporate (at least up to 10%) (Williamson 1994, 14; Hamrang 1994, 13) (Figure 2.8).

The resulting film is cut and stacked on top of each other to form a block (the blocking process) with a thickness of 5 to 6 inches. The blocks are pressed (about 1 ton/in.^{2}) in a hydraulic press at 95ºC, for several hours. In the end, the block and press are cooled. When finished, the block is transferred to a slicing machine where the sheets are cut and finally are polished (Williamson 1994, 13) (Fig. 1.8).

CDA was the first film base to be commercially used (Adelstein 2010, 389; Eaton et al. 1985, 40; Valverde 2005, 24). The first successful industrial production of CDA was carried out in 1905 by F. Bayer & Co.[43], known by its tradename *Cellit* (Rustemeyer 2004, 2). *Cellit* was the first CA film support to be used in 1912, being introduced in the 1920s by Kodak as support for 16mm motion picture film (Valverde 2005, 24). Later, in the 1930's other producers such as Agfa, Agfa/Ansco, Dupont, Dupont/Defender, Defender, and Hammer also produced CDA film-based negatives (Williamson 1994, 4; Valverde 2005, 24). As previously stated, the production of CDA film-based was gradually replaced by CAB and CTA, however Agfa/Ansco and Dupont kept producing CDA until 1955 (Valverde 2005, 24).

In this study's framework, besides the references to the trade name, initial use and the generic description, it was considered relevant to gather more information that could provide a broader understanding of this 'first CA' used as film support. Information gathered during the literature review and including the documentation accessed during a visit to the Agfa-Gevaert archive allowed for collecting in-depth information summarized on Table 2.9.

Table 2.9 – List of trade names, acetyl content and applications for *Cellit* product produced in different AGFA factories.

Name	Acetyl content (%)	Applications	Factory
Cellit T	61	Electrical isolations	I.G. Landsberg
Cellit M	**58**	**AGFA FILM and Röntgenfilm (X-ray)**	**Wolfen**
Cellit F	**56**	**AGFA FILM and Röntgenfilm (X-ray)**	**Wolfen**
Cellit K	54	Acetate silk and fibre	
Cellit LX	53.5	Lacquer manufacture	
Cellit L	52.5	Acetate sheet and moulded goods	Troisdorf
Cellit B	**42.5**	**AGFA FILM CAB (16.4% butyric acid)**	**I.G. Farben**

[43] The credits of commercial success of CDA are ascribed to G.W. Miller and F. Bayer since both discovered methods to obtain CDA. Discrepancies on the attribution are mostly related with dates of submission and acceptance of patents Worden (1916b, 2554).

From the documents found in the Agfa-Gevaert archive it was possible to conclude that *Cellit* was manufactured through the Dormagen process. According to data on Table 2.9, *Cellit B, F and M* were used as film supports. By comparing the data on Tables 2.6 and 2.9 it is possible to conclude that beside *Cellit B*, the *Cellit*'s F and M have a comparatively higher acetyl content than the range of values indicated for CTA on Table 2.6. Furthermore, it was not possible to conclude the timeline of *Cellit* films production. However, it is possible to suggest that during the 1920's to 1940's, CA polymer with high acetyl content was produced in Germany.

Regarding the production of the base for photographic negatives, a historical and detailed description of the processing conditions used to obtain films with different thicknesses was found:

> *This product is manufactured by flowing carefully filtered viscous solutions of the acetate in acetone onto a moving polished surface, and after evaporation of the solvent, continuously removing the film. Thickness down to 0.0002-0.0005 inch may be done. Films of greater thickness are made by solvent-lamination thinner gages, or by extrusion of pastes or plasticized pellets. Minimum amounts of solvent are used in paste extrusion of sheeting; the solvent must be well removed to secure a dimensionally stable product. High-temperature extrusion is now widely used where the plasticizers serve as the solvent at temperatures of 250-450°F* (c.120-230ºC). *Sheets, tubes, rods and articles of various cross sections are made by this process. Plasticizers, such as methyl, ethyl, or methoxyethyl phthalates, which are solvents for the acetate at high temperatures, must be used* (Malm and Hiatt 1954, 804–5).

According to the description given by Malm and Hiatt (1954, 804–5), the production of CDA sheets with '*greater thickness*' was complex and involved several steps that relied on temperature, solvents and plasticizers to obtain the desired thickness and physical properties. These technical manipulations may nowadays support the chemical and physical instability highlighted for CDA polymer and point out the accurate identification of such historical materials. Despite the difficulties found in identifying the production batches and correlate those with current film typologies present in film collections, this information was found relevant since it may contextualize some of the results obtained (see Chapter 4).

2.2.3.2. Plasticizers

Brittleness and thermal decomposition are two disadvantages pointed for CA polymer. By adding plasticizers, the melting viscosity and glass transition temperature decreases; while workability, flexibility and tensile strength are improved (Hamrang 1994, 22; Giachet et al. 2014). Although the ratio of plasticizers may change, the properties of the

polymer are improved by adding up to 20% v/v (Williamson 1994, 14). The plasticizer is adsorbed by the polar groups of the cellulose molecule forcing the separation between chains and reducing the number of hydrogen bonds and therefore reducing the molecular weight (Hamrang 1994, 23). This fact will improve the movement of the chains and consequently, the polymer becomes more flexible, in opposition to the stiffness of the cellulosic chain (Hamrang 1994, 23).

The range of plasticizers suitable for cellulose acetate is limited, especially considering that the volatility of some plasticizers does not allow their use in hot processing procedures (Hamrang 1994, 25). Walter E. Gloor[44] and C. B. Gilbert (1941) from the Hercules Powder Company, and Fordyce and Meyer (1940) from the Eastman Kodak Company presented a wide list of possible plasticizers (alone or mixed) for cellulose acetate and mixed esters, this contributed to improve the properties of the indicated CA polymers .

Dimethyl phthalate ($C_{10}H_{10}O_4$), diethyl phthalate ($C_{12}H_{14}O_4$) and triphenyl phosphate ($C_{18}H_{15}O_4P$) proved to be the suitable plasticizers for CA (Fig. 2.9) (Giachet et al. 2014, 224). Despite their compatibility with CA polymer, the volatility of the two former compounds is challenging and causes workability problems.

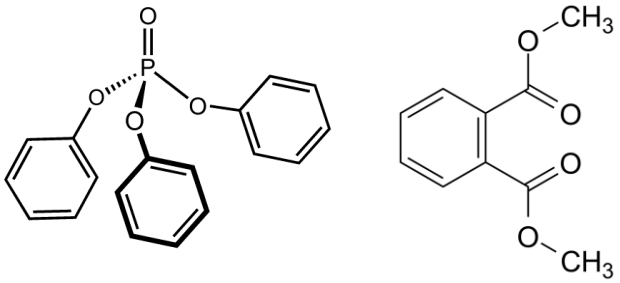


Figure 2.9 – Chemical structures of triphenyl phosphate (left) and dimethyl phthalate (right) (Shinagawa, Murayama, and Sakaiano 1992).

Triphenyl phosphate (TPP) was mainly used in a mixture with diethyl phthalate (Ballany 2000, 3,11). TPP was a successful plasticizer not only for CA but also for CN due to its flame retardant nature (Shashoua 2008a, 46; Hamrang 1994, 26). From the phthalates group, dibutyl phthalate ($C_{16}H_{22}O_4$) was also used as CA's plasticizer. According to the desired application, the phthalate and phosphate plasticizers mentioned are used in percentages ranging from 10 to 15 % of the weight of the polymer (Lavédrine 2003, 42). Regarding the plasticizers used for CAB polymer, di-n-hexyl adipate and di(2-ethylhexyl) succinate compounds are pointed out. Both are highly water resistance and non-volatile plasticizers. Additionally, according to the literature CAB requires less amount of plasticizers once this polymer has high dimensional stability and flexibility (Hamrang 1994, 17). These advantages result from the large side chains that improve their properties (Williamson 1994, 5). Thus, comparatively with CA polymer, the plasticizers

[44] Manager of the New Product Development Cellulose Products Department, at the Hercules Powder Company.

used to improve CAB polymer properties, are retained at higher concentrations and for prolonged periods of time. In part, the CAB-plasticizers system may be the main justification for the improved weathering characteristic of CAB polymer over CA polymer (Fordyce and Meyer 1940).

2.2.3.3. Other additives

Brief references to the use of stabilizers were found in the *British Intelligent Objectives Sub-Committee Report* (C22/ 1871; S.O. Code No. 51-3275.55) in which reference is made to the use of an anti-static treatment. According to the report, this treatment consisted in coating the films with solutions of MS (cellulose acetate-maleate-citrate by partial saponification) and/or MV (methyl polymethacrylate and polyacrylonitrile).

2.3 Still films structure: a brief description

All film-based negatives and motion picture films is composed by different layers. The number and thickness of the layers may differ according to the type of film (Ullmann 1992, 132).
A common cross-section for still film negatives is presented in Fig. 2.10.

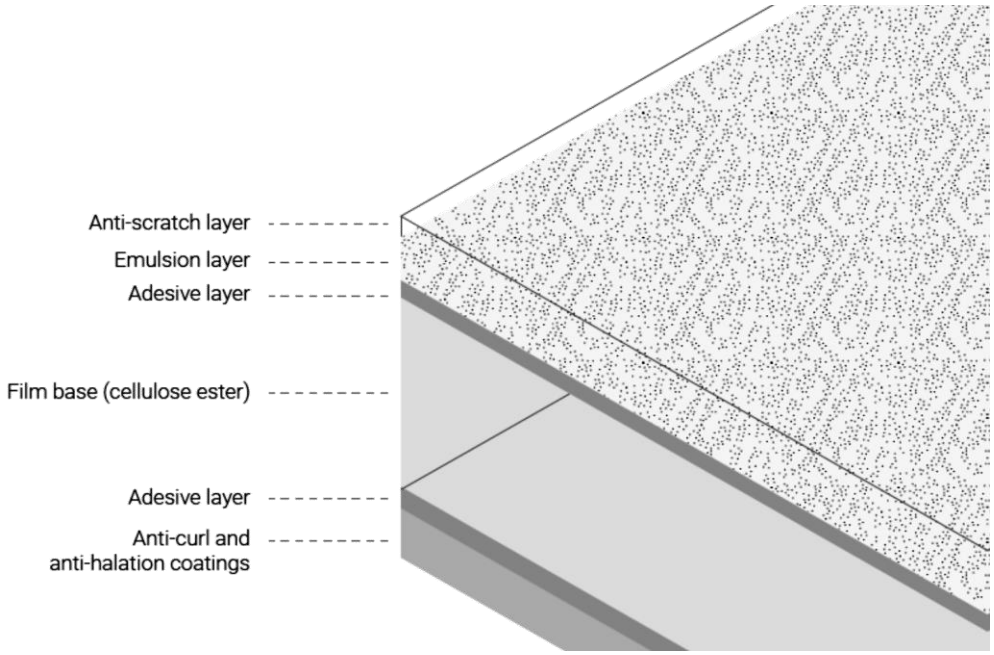


Figure 2.10 Cross-section of cellulose esters film-based negatives (adapted from Adams 2005, 16).

The typical layers existing on films are the base (cellulose esters), the photographic emulsion (gelatine/silver bromide) and the subbing layer (Valverde 2005, 20–21, 24–25; Ullmann 1992, 132).

The anti-halation and anti-curling layers were used depending on the type of films (Glafkidès 1949) and periods of production (Valverde 2005, 21). Therefore, the film's thickness results from the number of layers present (Neblette 1952c, 161; Ullmann 1992, 132). Thickness also varies according to the film's formats and photographic applications (Neblette 1952c, 161) (see Table 2.3). As Peter Adelstein (2010, 395) wrote

> *It should be noted that there can be no such thing as a universal film support since the properties required in one product line can sometimes be detrimental in another*.

Therefore, differences in the composition and thickness of the films are expected.

2.3.1. The photographic emulsion

A photographic emulsion consists of a dispersion of silver halides[45] (AgX) in a colloid (Neblette 1952c, 118). As already said, plastic negatives have a gelatine silver-bromide emulsion, with a small percentage of silver iodide (Neblette 1952c, 118).
In Chapter 1, the unquestionable success of gelatine emulsions presented emphasized its widespread use since the late 19th century. The success of the gelatine as an emulsion medium relied on its chemical and physical properties (Neblette 1952, 118; Williamson 1994, 30; Mees 1942, 59).
From the several gelatine properties that could be mentioned, those of interest to produce photographic emulsions are:

- the amphoteric nature that relies on the gelatine's chemical and physical properties (chemically reactive);
- the thermo-reversible transition from hydrosol to the hydrogel (gel properties);
- the controlled swell state and permeability that allows the rapid diffusion of developing solutions;
- the indirect contribution to the size and shape of silver halides (slow rate growth of the crystals yielding flat palettes);
- the capability to provide a homogeneous distribution and protection to silver halides (protective colloid function);
- the contribution to the increase of light sensitive silver halides (due to the presence of sulphur containing compounds, e.g. cystine, that act as sensitizers);
- the transparency and colourlessness;
- the purity;
- the capability of being easily applied over a substratum.

[45] Halide results from the combination of the halogens chlorine (Cl^-), bromine (Br^-) and iodine (I^-) with an elemental metal like potassium and sodium. The photographic halides are chlorides, bromides and iodides, which combined with elemental silver or silver nitrate result in a silver halide (Osterman and Romer 2007).

Gelatine is obtained by partial hydrolysis of collagen[46] (Schrieber and Gareis 2007, 45). Two methods are used to obtain gelatine: the acid-process (gelatine Type A) and the alkali-process (gelatine Type B) (Schrieber and Gareis 2007, 68). Photographic gelatine is generally produced by the alkali-process (Type B) (Schrieber and Gareis 2007, 61).

The treatment is performed by treating collagen with the aforementioned processes at different ranges of temperature, during weeks or even months. From the collagen's treatment results the cleavage of intermolecular bonds, being obtained gelatine. The gelatine obtained has a molecular weight (M_w) ranging between 15000 and 25000 g mol^{-1} (Schrieber and Gareis 2007, 48; Johansen 2004, 9).

Gelatine is composed of amino acids linked together and forming polypeptide chains. The sequence of amino acids in the polypeptide chain is not known. However, it is known that the primary compounds present in the chain are glycine, proline, and hydroxyproline. Gelatine is an amphoteric material, with acidic and alkaline properties, due to the presence of both carboxylic (acid) and amine (alkaline) groups. Therefore, the gelatine's properties are pH-dependent (Glafkidès 1987a, 393).

The surface activity of gelatine is explained by its isoelectric point (Alleavitch &Turner 1990; Schrieber & Gareis 2007). At pH values close to the isoelectric point, there is no charge development in the amino acids, being described as a neutral gelatine. Changes of pH lead to changes on the electro activity of gelatine, thus whenever pH increases, gelatine becomes negatively charged, and in opposition when pH decreases gelatine becomes positively charged (Schrieber and Gareis 2007, 61). Near the isoelectric point gelatine molecules are arranged in a random coil structure (Schrieber and Gareis 2007, 61). Changes in pH will lead to conformational changes resulting in an unfolding of the molecule caused by charge repulsion, and in consequence gelatine swells (Schrieber and Gareis 2007, 61; Johansen 2004, 9). The characteristic isoelectric point for photographic gelatine (Type B) ranges between pH 4.7 and 5.2; however, values may vary depending on the components and pre-treatment of collagen (Johansen 2004, 9).

Among other parameters, the selection of gelatine Type B for the production of emulsions relied on the increased viscosity, by comparison with gelatine Type A (Schrieber and Gareis 2007).

Concerning gelatine's stability, the solubility and swelling behaviour is a concern whenever it is considered that photographic emulsions are submitted to photographic

[46] Collagen is a protein obtained from treatment of animal's bones and hides. Collagen has multiple peptide chains, composed by α-amino acids, with a three helical conformation that result from intermolecular cross-links, resulting in a triple helix structure (Mees 1942, 60; Alleavitch and Turner 1990, 3; Schrieber and Gareis 2007).

processing with diverse types of solutions (developing solutions[47], stop bath[48], fixing solutions[49], water[50]) and different processing conditions (temperature, pH). In order to prevent losses of the gelatine emulsion, hardening reagents are added to the gelatine to change its rheological behaviour (Schrieber and Gareis 2007, 116). For that purpose, several compounds are used to perform a crosslink of the gelatine and to develop a protective coating for the photographic emulsion. The common hardeners used are organic crosslinkers (e.g., aldehydes and ketones), or inorganic crosslinkers (Al^{3+}, Cr^{3+}, Cu^{3+}, Fe^{3+}, Th^{4+}, Zr^{4+}, Ti^{4+}, Ce^{4+}, U^{2+}) (Mees 1942b, 100–126; Glafkidès 1987a, 544–47). The hardening treatment results in increased viscosity, higher melting point, decreased swelling ability and improved resistance to mechanical stress (Mees 1942b, 100).

2.3.2. Anti-curling layer

The anti-curling layer consists of a layer of gelatine hardened coated on the back of the plastic support. This layer is applied with the aim to counteracting the tension caused by gelatine from the photographic emulsion and maintain the negative flat (Valverde 2005; Glafkidès 1949) (see Fig. 2.10).

2.3.3. Anti-halation layer

The anti-halation layer acts as a filter that prevents silver salts from absorbing the radiation reflected by the support (Glafkidès 1987b, 759; M. F. Valverde 2005, 21). Commonly, anti-halation dyes are added to the anti-curl gelatine (Neblette 1952c, 154). The features necessary for non-halation dyes were summarized as follows (Neblette 1952c, 155):

1. Dyes should have *high light absorption* (especially in the region of highest sensitivity of the emulsion);
2. The dyes should not have a deleterious effect on the gelatine and neither on cellulose ester base;

[47] A developing solution consists of an aqueous solution with a mixture of chemical compounds that will react with the silver halide closer to the latent image (Ag^+) to the final metallic silver image. The chemical compounds used in developing solutions are: a) developing agents (metol (4-hydroxy-*N*-methylbenzenaminium hydrogensulphate), phenidone (1-phenyl-3-pyrazolidinone), dimezone (4,4-dimethyl-1-phenylpyrazolidin-3-one), hydroquinone (benzene-1,4-diol); alkaline agents (sodium carbonate, borax, sodium hydroxide); anti-oxidizing agent (sodium sulphite, Na_2SO_3); developer restrainer (potassium bromide, KBr) (Melo 1987).

[48] The stop bath is used to halt the development of the image. Commonly, an aqueous solution with a weak acid (e.g. acetic acid) is used (Melo 1987).

[49] After developing the image, it is necessary to stabilize and fix it. The fixation bath contains sodium or ammonium thiosulphate ($Na_2S_2O_3$ and $(NH_4)_2S_2O_3$, respectively), sodium sulphite (Na_2SO_3), acetic acid (CH_3COOH) and boric acid (H_3BO_3). In the fixing process, unexposed silver halides are removed through complexation of the silver ions with thiosulphate while metallic silver is kept (Melo 1987).

[50] The development is finished with a washing step, in which water is used to remove soluble salts from the fixing step left as residues in the gelatine (Melo 1987).

3. They should not react with the developing agents;
4. They should be completely removed or bleached in the developing or fixing bath;
5. They should not leave residues after photographic processing.

According to Neblette (1952b, 155), triphenylmethanes such as acid fuchsin ($C_{20}H_{17}N_3Na_2O_9S_3$) and malachite green ($C_{23}H_{25}N_2$) were the most common non-halation dyes used.
Moreover, Pierre Glafkidés (1987b, 760) correlates the anti-halation dyes with types of photographic emulsion. According to this author, acid fuchsin (associated with pink colour) was mostly used in orthochromatic emulsions while the green sulfo, methyl green, acid green or Helvetia dyes were used in panchromatic emulsions.

2.3.4. Subbing layer

With different polarities, it was necessary to apply an adhesive layer to promote the long-term adhesion between the photographic emulsion layer and the film base. In general, the subbing or adhesive layer described has been made up of mixtures of gelatin with CN or CA polymers, dissolved in organic solvents and water. A thin layer of adhesive is applied over the surface of the film base, followed by the application of the photographic emulsion layer (Neblette 1952c, 170). Besides the general description of the materials and method, a specific reference on the composition of the adhesive layer used for CDA was found. According to Glafkidés, chrome alum ($KCr(SO_4)_2$) salts were added to the aforementioned adhesive (Glafkidès 1949, 275–93). The reason for doing so was not clarified however it is believed that chrome alum might be used as a gelatine hardener and to improve adhesive properties.

2.3.5. Film thickness

As reported in the literature, plastic negatives have different thicknesses varying according to types of films and requirements (see Chapter 1, Table 1. 3).
Table 2.10 was designed during this study and summarizes the common thickness of CA and CN film-based negatives according to standard formats.

Table 2.10 - Common thickness for CA and CN film-based negatives with different formats (Calhoun 2010, 371; Neblette 1952c, 152)

	Common thickness			
	CA film		CN film	
Film formats	inches	mm	inches	mm
Roll film	0.0033	0.085	0.0035	0.089
Motion picture	0.0055	0.14	0.0055	0.14
Sheet film	0.0083	0.210	0.008	0.203

Considering that this work is focused on historical film-collections, it was also relevant to know the thickness of film-based negatives and to confirm if there were any differences on the thickness according to the type of base.
Given the data presented on Table 2.10, CN and CA film-based negatives have a similar thickness which is established according to the formats.
Nevertheless, according to the literature there are differences in the thickness of each layer that is present in film-based negatives (Ullmann 1992, 132). A summary of those differences is illustrated in Fig. 2.11.

Figure 2.11 – Scheme of a cross-section of b/w film-based negatives and thickness of each layer: a) overcoat (0.2-1.0µm); b) panchromatic emulsions (3-12 µm); c) subbing layer (< 0.3 µm); d) cellulose ester base: 170 – 200 µm (sheet film), 90-100 µm (roll film); 115-130 µm (films 135, 126, 110 motion-picture film); e) anti-halation layer (2-5 µm) (adapted from Ullmann 1992, 132).

In Figure 2.11 it is possible to see that the film base has the higher thickness followed by the photographic emulsion and anti-halation layers, respectively.

2.4 Image processing and image improvements

After exposure, the image is kept on a latent state. Through photographic processing, the silver halides sensitized are converted into metallic silver (visible image) and the unexposed silver halides are removed. In a broad sense, photographic processing consists of developing, fixing and washing the image.
However, other optional steps such as chemical corrective treatments of the image (Fig. 2.12), retouching/varnishing, and masking corrective treatments (Fig. 2.13) could be performed (Valverde 2005, 15–16, 20–21, 25).
It was common to correct an image, which lacked density and contrast. For that reason, the photographers performed chemical corrective treatments to improve the quality of the image (Mees 1942b; Neblette 1952c; Lavédrine 2000b, 277).

Figure 2.12 - CN film based-negatives chemically treated with intensification and reduction solutions (top and bottom, respectively), from ECC collection. © AHU-DGLAB/Credits: Élia Roldão.

Figure 2.13 - Example of CN film-based negative with a red ink mask, from the ECC collection. © AHU-DGLAB/Credits: Élia Roldão.

Generally, two types of methods were used to correct the images' density and contrast: the intensification and the reduction methods (Mees 1942b, 542–61; Neblette 1952c, 351–63) (Fig. 2.12). The chemical solutions used contained diverse types of compounds and the effectiveness of the action was dependent on those (Neblette 1952c, 351–63; Mees 1942b, 542–61; Glafkidès 1987a, 222–37). An overview of intensification and reduction methods and diverse solutions used in each method is presented in Appendix I. Later, all the data collected regarding intensification and reduction methods will support the results obtained during the visual and molecular assessment of film collections studied (please see Chapter 6).

Besides chemical treatments, photographers retouched masked and coated the negatives to provide protection or for practical functions (e.g. correction of flaws) (Norris and Kennedy 2005, 13). More information about these actions is presented in Appendix I.

2.5 Degradation

What are the major factors which influence the stability of photographic film? (Edge et al. 1989, 345)

This section provides an overview of the common degradation pathways of cellulose esters as an attempt to shed light on the mechanisms behind the decay as on the visible symptoms in which the macro assessment of collections relies on, an issue that will be addressed in Chapter 6.

Besides the degradation of the cellulose ester base, other issues must be addressed in order to emphasize the complexity of the degradation of the CN and CA film-based negatives. As shown in section 2.3, film-based negatives are composite materials. Each layer contributes for the stability or, in an opposite situation, for their degradation of the support. The contributions of manufacture conditions, plasticizers, gelatine emulsion, subbing layers and photographic processing are briefly summarized in this section. Additionally, the contribution of storage materials to the degradation of negatives is also addressed. An insight of both intrinsic and extrinsic degradation factors of chemical and physical decay of plastic negatives will support the discussion of the results achieved on the visual and molecular assessment of the film collections studied (Chapter 6).

2.5.1. Degradation of cellulose nitrate

"Nitrate is still waiting for history's verdict, and it'll be a long time coming"
(Leo Enticknap as cited in Heckman 2010, 484)

CN polymer is regarded for its high flammability and chemical instability (Adelstein 2010, 388), thus investigations have been mostly focused on thermal degradation (Wolfrom et al. 1955; Dauerman and Tajima 1968; Jutier et al. 1987; Brill and Gongwer 1997; Rychlý et al. 2012). Concerning the conservation of design and artworks made with CN polymer the action of light and temperature on the decay of such artifacts was also investigated (Sirkis 1982; Derrick et al. 1993; Quye et al. 2011; Berthumeyrie et al. 2014; Bussiere et al. 2014). The action of light and temperature on CN adhesives used for conservation treatments has also been studied (Koob 1982; Shashoua et al. 1992). Recently, it was concluded that the polymer undergoes similar thermal and photodegradation rates (under the illumination conditions used, $\lambda>295$ nm); however, light has a higher detrimental effect (Berthumeyrie et al. 2014; Thérias et al. 2012). Besides photochemical and thermal degradation, CN polymer undergoes hydrolytic degradation reactions (Hamrang 1994, 54).

It is believed that the primary decomposition process starts due to thermal sensitivity of CN polymer (Hamrang 1994, 54; Edge et al. 1990, 630). At a first stage, the polymer denitrates or in other words the nitrate ester groups on C2 and C3 positions split off from

the cellulose molecule (homolytic scission of CO-NO_2). This phenomenon is supported by the fact that , comparatively, the CO–NO_2 bond at C2 and C3 positions has lower bond energy (163 kJ mol^{-1}) than at the C6 position (330 kJ mol^{-1}) (Hamrang 1994, 54; Shashoua 2008a, 178; Rychlý et al. 2012, 1274). Regarding, the C–C (347 kJ mol^{-1}), C–O (360 kJ mol^{-1}), and C–H (414 kJ mol^{-1}) bonds, these have higher bond energy dissociation than CO–NO_2 bonds (Edge et al. 1990, 623).

From this initial reaction, the formation of NO_2, aldehydes, ketones and alcohols can take place (Sirkis 1982, 24; Hamrang 1994, 54; Stewart 1997, 18). Also, from this primary decomposition, a chain length decrease of the polymer may occour (Hamrang 1994, 54). If not removed, the formed degradation products will lead to an exponential degradation process (autocatalytic point) through oxidation and nitrosation reactions, hydrolysis of further ester groups and hydrolytic scission of the cellulose chain (Edge et al. 1990, 623; Stewart 1997, 18). These reactions rely on the presence of oxygen and moisture on the storage room. The nitrogen dioxide reacts with moisture and oxygen forming nitric acid that will induce additional denitration, hydrolysis of cellulose chain and oxidation of the cellulose units (Ott 1943, pp643 as cited in Sirkis 1982, 24). The chemical breakdown (de-esterification and chain scission) may occur due to acidic or alkaline hydrolysis (Hamrang 1994, 58,62). Along with chain-scission, hemiacetal and aldehyde groups are produced. From the continuous release of NO_2 a 'highly oxidizing atmosphere' is formed and consequently carboxylic acid groups are produced. Furthermore, in the presence of metal ions a fast oxidative decarboxylation occurs (Hamrang 1994, 63). The acids formed speed the degradation reaction and induce further decomposition of the polymer.

Thus, internal factors such as raw materials (described previously), solvents, manufacturing process, fillers and plasticisers contribute to the degradation or stabilisation of the polymer. Yvonne Shashoua[51] (2008a, 10) also pointed out age and experimentalism as causes for CN decay by writing:

> *Instability of the earliest plastics, cellulose nitrate and cellulose acetate is expected due to their poorly stabilised formulations and because they are the oldest man-made plastics in museums.* (Shashoua 2008a, 10)

Regarding the contribution of moisture for CN decay, different opinions were found, one indicates that dinitrates are very resistant to water (Sirkis 1982) and another mentions that CN is a highly polar polymer, and therefore more unstable (Selwitz 1988, as cited in Reilly 1991, 155). However, the correlation between moisture absorption and decay does not seem to be linear. References on different rates of moisture absorption for celluloid and highly nitrated CN polymers were indicated, note that the former is more susceptible to moisture (Reilly 1991, 1955). Additionally, it may also be referred that the moisture

[51] Senior Researcher in Modern Materials at the National Museum of Denmark.

content of the film (including emulsion layer) may induce further degradation by reacting with nitrogen dioxide and form nitrous and nitric acid (Edge et al. 1990, 623).
In Fig. 2.14, examples of CN films with different conservation grades are shown. The two CN film-based negatives shown are one in Good condition (top) and the other is severely degraded (bottom). From this image is possible to understand the extent of degradation that might be found in CN based negatives.

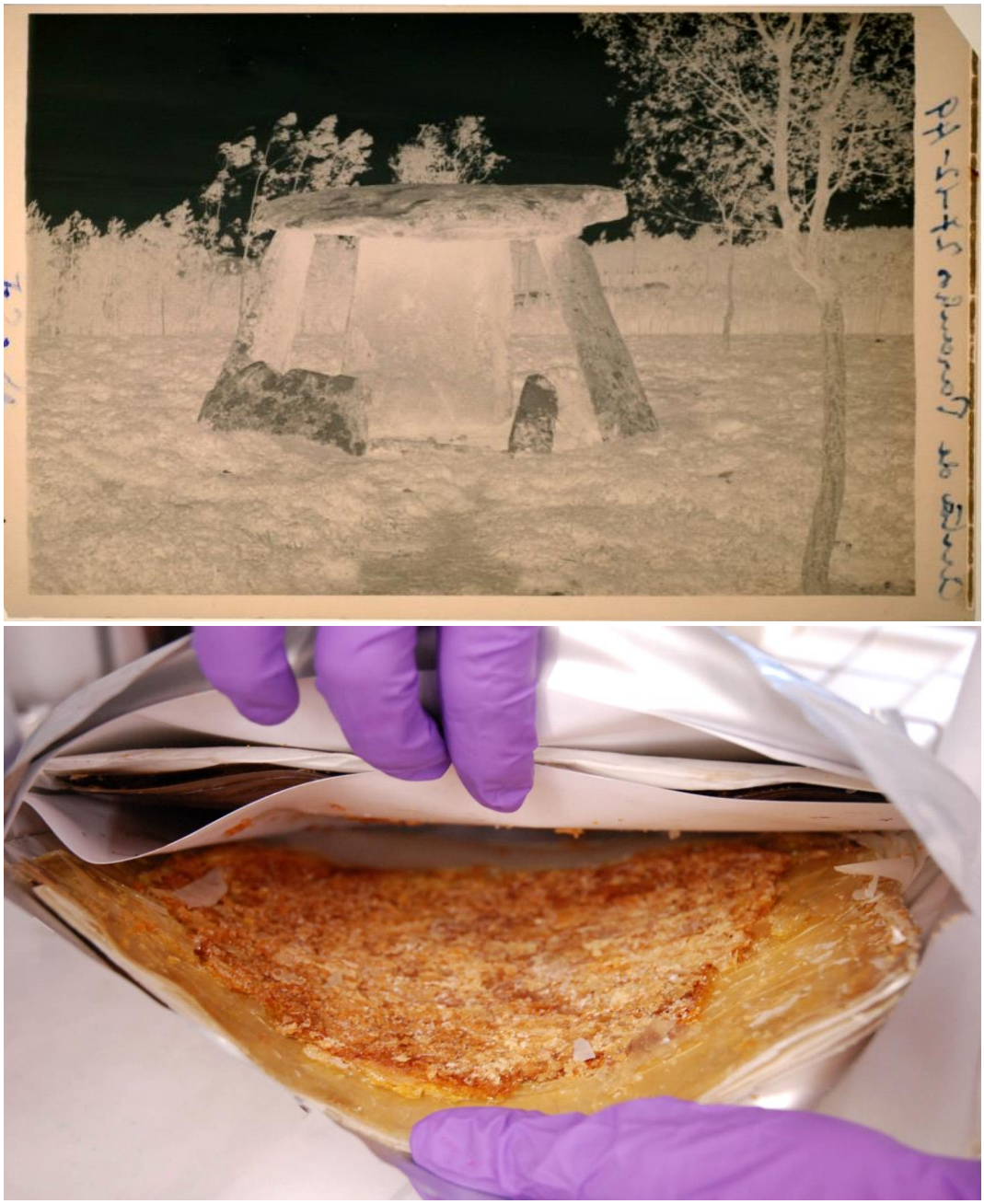


Figure 2.14 – CN film-based negatives with different conservation grades. Top: the overall image of a negative in Good condition (top), from DGEMN collection. © SIPA-DGPC/Credits: Élia Roldão. Bottom: overall view of a set of negatives severely degraded (showing intense brown colour, and stick among them and to enclosures), from the Mário Novais collection. © BA-FCG/Credits: Élia Roldão.

2.5.1.1. The role of thickness on the degradation CN film-based negatives

Although CN is intrinsically unstable the degradation process is different according to the type of object (Stewart 1997, 17).
In the field of conservation of photographic materials, different behaviours of CN film-based negatives were noticed. According to the literature, there is a correlation between thickness and degradation, which suggests that CN film-based negatives with thicker supports, such as sheet films, are more prone to degrade than thinner films (Calhoun 2010, 371; Williamson 1992, 6). For instance, J. M. Calhoun[52] (Calhoun 2010, 371) wrote that:

> *The difference in base thickness between these several types of film is of practical importance in nitrate film storage because the thicker the base, the greater the amount of cellulose nitrate in the film. The thicker films are more hazardous and more likely to decompose with age.* (Calhoun 2010, 371)

Eugene Ostroff[53] (2010, 10) corroborates the theories of the former authors by indicating that degradation results from the acidic products (gases) trapped in thicker films.
CN is a tricky polymer since it still lacks agreement on the degradation mechanism. Additionally, composite materials show differences in degradation mechanisms and degradation rates that demand further investigations.

2.5.2 Degradation of cellulose acetate

Cellulose acetate deterioration is commonly associated with acidic hydrolysis (Ram 1990; Allen et al. 1988; Edge et al. 1989).
Figure 2.15 shows two examples of CA film-based negatives in Fair degradation condition (left) and another severely degraded (right).
Hydrolytic degradation was reported as the initial degradation route for CTA photographic film stored under archival conditions (Allen et al. 1988). Hydrolysis consists on the cleavage of acetyl groups from the main chain by reaction with moisture, leading to deacetylation of CA with the formation of acetic acid.

[52] Described as 'an earlier pioneer of photograph preservation', during the time he worked at Kodak, Calhoun conducted several researches focused on degradation and preservation of film-based negatives.
[53] Eugene Ostroff (6 July 1928 – 26 August 1999) was a historian and curator of the Photographic History Collection at the National Museum of American History.

Figure 2.15 –CA film-based negatives with different conservation grades. One in Fair condition (left) and another severely degraded (right). The image on the left is from Silva Nogueira collection and the image of the right is from San Payo collection. © ADF-DGLAB/Credits: Luísa Oliveira.

Initially, the acid formed is retained in the polymer chain and it will gradually diffuse into the atmosphere, causing the typical vinegary smell (*Vinegar syndrome*) (Ballany et al. 2001, 146). Under adverse conditions, acetic acid formation starts at a slow and continuous rate (induction period). However, if the acid is not removed, the acid content increases exponentially to drastic proportions, reaching the auto-catalytic point (Reilly 1993, 10–13). This process is favoured because of the high solubility of cellulose acetate in acetic acid, leading to a gradual destruction of the polymer structure. The hydrolysis of cellulose acetate is induced by high relative humidity, temperature and pH (acid or alkaline) and the rate of the reaction is dependent on the intensity of the factors present (Edge et al. 1988, 200–201). Figure 2.16 presents a scheme of CA deacetylation.

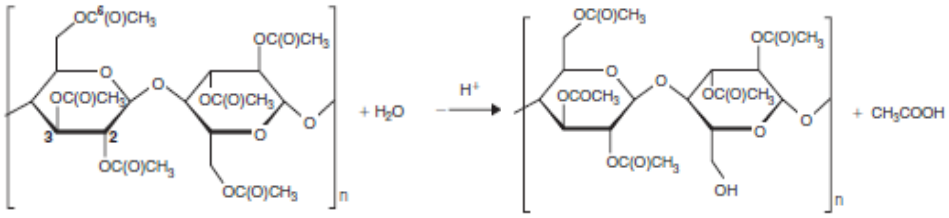


Figure 2.16– Deacetylation reaction for cellulose acetate polymer (Shashoua 2008, 182)

The loss of the acetyl groups is not random. According to Derham *et al.* (1992, 132) the deacetylation occurs in the following sequence: C6 (fast) > C2 (slow) > C3 positions of the glucose. This phenomenon was unexpected since C2 and C3 are secondary and C6 is

a primary position. However, by NMR spectroscopy C2 and C6 have proven to be the most reactive and exposed positions, being the first to convert hydroxyl groups to acetyl groups during the cellulose esterification. Thus, in a reverse process, these are the first to be hydrolysed during degradation process (Derham et al. 1992, 135). On the other hand, with time polymers tend to polarize, thus becoming more hydrophilic.
In sum, CA decay involves the following reactions (Ram 1990, 18–24; Edge et al. 1988, 200):

a) Hydrolytic deacetylation, which results in acetic acid formation. If not removed, acetic acid will increase the degradation process.
b) Chain-scission of the polymer, resulting in loss of viscosity and physical properties.
c) Ring opening.

The activation energies necessary for chain-scission are higher than those for cleavage of the side groups. Nevertheless, the increasing formation and presence of degradation products will lead to chain-scission (Ram 1990, 20–21). This rupture will result in a decrease of the polymer's molecular weight, and consequently in the loss of physical properties (Adelstein et al. 1995a). Moreover, an increase of viscosity, insolubility and moisture are also reported as a consequence of CA's chain-scission (Allen et al. 1987). A decrease in pH is also correlated with CA's decay (Adelstein et al. 1995a). Thus, as the degradation process evolves the film based-negative loses elasticity and becomes more brittle. CA film-based negatives become yellow due to the formation of carbonyl, ketone and aldehyde groups (chromophores).
Furthermore, CA's polymer DS is reported as a crucial fact to understand CA's decay, specifically considering CDA polymer (DS=2). According to Diana Michelle Williamson's study on CA motion picture film (1994, 4), CDA has lower physical and chemical properties, which would make it more vulnerable to the action of external factors, such as moisture. Moreover, by comparing the moisture absorption rates for CA polymers it was found that CDA has a higher absorption rate (Ram 1990, 16) (Table 2.7). Therefore the rate of hydrolysis of CDA will be higher than that of CTA (Edge et al. 1988, 200) (Table 2.7, page 46).

The contribution of photographic processing solutions (pH and redox nature of the components) to CA film-based negatives decay was also investigated. It was concluded that sulphuric acid and chromic potassium sulphate have a detrimental effect on CTA film (Edge et al. 1989, 347).
A focus on the contribution of the CN subbing layer for the degradation of CDA still film negatives was also given (Orraca 2010, 32). According to the literature, *nitric oxide gases* (NO_2 and HNO_3) are generated by hydrolytic degradation of CN subbing-layer. The gases are trapped between the support and the emulsion layers and overtime induce the acid-catalysis of CA (Ram and McRea as cited in Williamson 1994, 52). Additionally, José Orraca presented the hypothesis of thicker CN subbing layers speed the degradation of CDA

films, e.g. in Defender films. However, this issue is not clear (Norman S. Allen et al. 1989, 347; Edge et al. 1989).
Besides the discolouration of CA polymer itself, blue and pink discolourations may occur due to acidification of the CA film support. According to Reilly (1993), the rise of these discolourations is a direct consequence of acetic acid formation that will regenerate the anti-halation dyes. Furthermore, Horvath (1987) points out to the presence of mould on the surface of the negatives as another cause for discolouration of CA negatives.

2.5.3 The role of plasticizers in the degradation process

As previously mentioned, plasticizers play an extraordinary role by improving the physical stability of cellulose derivatives and by preventing the uptake of moisture by those polymers. Nevertheless, overtime, it was found that plasticizers play a role in the degradation of cellulose esters. Used in different ratios (20-30% by weight of the polymer), plasticizers are volatile and therefore (because of their migration from the polymer molecule) the artefacts tend to distort (Hamrang 1994, 69).
Camphor's sublimation at room temperature is pointed out as one plausible cause for CN physical breakdown (Shashoua 2008a, 177). The loss of plasticizer results in the formation of cracks and crazing, which will allow the diffusion of the plasticizer and the absorption of moisture from the ambient, inducing further degradation (Stewart 1997, 19). In an opposite situation, it was referred that phosphates and phthalates used to plasticize CN (see section 2.2.2.1) absorb acidic products resulting from CN degradation (Shashoua 2008a, 177). Nevertheless, it is important to keep in mind that in opposition to moulded objects, photographic emulsion and anti-curling layers in part may protect the film base from absorbing moisture or in a opposite situation, it may provide moisture.
Regarding CA, according to studies carried out in 1990's, unplasticized CTA is more stable (Shinagawa, et al. 1992, 142–45). However, since commercial CTA was plasticized with phosphate and phthalate plasticizers, the contributions of these on CTA degradation have been studied. It was concluded that the former has a detrimental effect on CTA. In particular, the action of triphenyl phosphate (TPP) was investigated. According to the results, it was suggested that CTA plasticized with TPP tends to degrade more due to excessive amounts of TPP used or due to the degradation products resulting from TPP chemical decay, e.g. diphenyl phosphate (DPP) and phenol. These two degradation products are indicated as triggers for CTA acidic hydrolysis (Shinagawa et al. 1992, 146–47). Other authors suggest that the recrystallization of TPP acts as a *nucleophilic catalyst* and thus induces CA degradation (McGath 2012). In sum, the chemical decay and loss of plasticizers is also associated with the degradation mechanism of CA polymer. As the polymer degrades, it loses capability of retaining the plasticizer in the matrix, which results in its migration to the surface of the polymer. The plasticizer migrates and recrystallizes between the film support and the photographic emulsion. These exudations may occur in the form of needle-like crystals or liquid (trapped inside bubbles) usually

concentrated in the centre of the object (Hamrang 1994, 69; Valverde 2005). The loss of dimensional stability and physical property decay, in part, also results from the loss of plasticizer (Reilly 1993, 12; Richardson et al. 2014b). However, TPP is also regarded as an antioxidizing agent which prevents CTA decay (Edge et al. 1989, 348). Therefore, to some extent plasticizers may act as stabilizers.

Regarding the importance of knowing the degradation factors to preserve photographic collections, in 1967, Eugene Ostroff, a curator of photography, wrote:

> *Pictures are in constant danger of attack by various contaminants. Although some photographic processes demonstrate exceptional stability, none is completely resistant to all environments.* (Ostroff 2010, 8)

This sentence still reflects the current need of investing in research that supports the development of new methods for identification, assessment and monitoring of large film collections.

Chapter 3

Currently used methods for identification and assessment of degradation of cellulose ester photographic negatives: an overview

Chapter 3 – Currently used methods for identification and assessment of cellulose ester photographic negatives: an overview

"In the nineteen-thirties, the increasing use of photographic film for archival records and the expanding entertainment industry stimulated interest in the issue of permanence."

Jean-Louis Bigourdan, P. Adelstein and James M. Reilly (1998, 3)

Along with the scientific and technical development of film-based negatives and motion picture films in the 19th and 20th centuries, several methods have been proposed to perform the identification and assessment of cellulose ester film supports. Besides the manufacturer's, several research centres and conservation laboratories have proposed and published simple methods for identifying and assessing cellulose ester film supports. In this chapter a thorough survey of literature specifically focused on the conservation of film-based negatives, motion picture film and the industry of plastics was analysed.
The importance of identifying the film supports and preserving collections of still film negatives and motion picture film will be discussed and different classes of identification methods will also be presented. The various categories of identification methods will be established based on selected parameters such as technical aspects concerning the manufacturing processes, which endorse a visual identification of the base material through destructive and non-destructive tests. In addition to identification, the degradation assessment methods currently used in archives and museums will be analysed. Further discussion on the pros and cons of each method will be presented to promote debate on the accuracy of the present methods used in conservation labs and archives on a routine basis.

3.1 Introduction

Throughout the late 19th and 20th centuries, manufacturers made efforts to develop new and stable products (Adelstein 2002, 53; Brems 1988, 992). At the time, manufacturers and retailers provided information about photographic products in photographic manuals and catalogues (Pritchard 2008, 9). In the late 19th century, the increasing release of photographic journals allowed sharing the scientific and technical knowledge in respect to photographic materials and photographic practices (Osterman 2007, 31,102). Since the 1890s, manufacturers increasingly invested in the advertisement to commercially promote their brand (Pritchard 2008, 9). Nowadays, advertisement, film

packages, photographic manuals, retailer's catalogues, photographic journals and photo-lab index (retailers' catalogues) are incredible sources providing useful information about the variety of photographic products commercially produced by the main manufacturers. Figs. 3.1 and 3.2 are examples of the information available in photographic magazines and film-based negatives packages.

Figure 3.1 Cover page(left) and an advertisement page of photographic materials (right). Images adapted from 1905s Portuguese photographic magazine, BOLETIM PHOTOGRAPHICO.

Figure 3.2 Examples of roll film packages of different producers (Agfa, Ferrania, SELO and Kodak) in which brands and technical information are disclosed. © Élia Roldão.

In part, the selection of materials relied first on the information available in the aforementioned sources. As is possible to observe in Fig. 3.2, technical aspects of the films were given in film packages. The description of the support type became paramount since the report of fires caused by CN film (Heckman 2010, 494). The reference to *"safety film"* was a clear indication to CA film supports, a more stable film (Figs. 3.2, a package of the Kodak Plus -X Safety film).

Furthermore, insightful information regarding types of photographic films and specific applications (e.g. fashion, art, military use, etc.), photographic processing, among other technical subjects are also available in photographic magazines (Fig. 3.1) and Photo-Lab Indexes[54] (Lester 1946; Lester and Carrol 1956).

The versatility and enormous use of flexible films during the 20th century is reflected in archives filled with plastic negatives demanding preservation strategies based on accurate identification and assessment of film supports.

Besides the investments made to advertise and on products disclosure and photographic procedures, some producers also launched researches to understand degradation paths for the different film supports (Adelstein 2002, 53). The performed research resulted in published guidelines for conservation and preservation of film-based negatives, motion picture film, and X-ray sheet films (Eaton *et al.* 1985; 1992a; 1992b; 1995a).

Furthermore, information related to film decomposition was gathered and compiled by collections holders, archivists and photographs conservators (Horvath 1987; Fischer & Robb 1993; Lavédrine 2008) aiming to support decision-making processes during the preservation of photographic collections (Fischer 2012; Fischer & Robb 1993; Horvath 1987; Lavédrine 2008). The main goal of the present chapter is to clarify the most commonly used film identification and assessment methods currently applied by archivists and conservators and to launch new perspectives for the strategic preservation of film collections.

3.2 Simple identification methods

Flexible film was profusely used for still photography and cinema since the late 19th century and during the entire 20th century (Read and Meyer 2000, 1; Adelstein 2010, 385). Photographs and cinema archives have enormous quantities of plastic negatives and motion picture films (image and sound, negative and reversal film). Visually, films are similar whenever there are no embossed marks or degradation patterns that distinguish them. However, since the acidic decomposition of a single film can contaminate and catalyse the degradation of surrounding film collections, identifying the composition of

[54] This research considered visiting institutions that held archival documentation from European manufacturers that could support some of the issues proposed in this investigation. Therefore in 2015 two institutions were visited: the Agfa-Gevaert archive and the Museum of Photography of Antwerp (FOMU) library. The two Photo-Book Indexes were consulted in FOMU library.

film supports is extremely important to ensure the preservation of such heritage. A film manufacturing and discontinuation chronology provides a baseline to distinguish types of film supports (Valverde 2005). Additionally, visual observation of edge printing and dating information, performing destructive tests and analysing degradation patterns are commonly applied to ensure an accurate identification (Lavédrine 2008; Fischer & Robb 1993; Valverde 2005).

3.2.1. Dating information

Dating information offers broad periods of time, allowing to contextualise the production and use of film supports (Valverde 2005; Lavédrine 2008; Eaton et al. 1985; Read & Meyer 2000) (see Table 2.2). Archivists, collectors, historians and conservators use this data to perform a first level identification of the film supports.

Regarding the production periods for still photography negatives and motion picture film, the information available in the literature expands on knowledge of film productions periods; however, it is mainly related to the production carried out in the United States of America, including brands as Kodak, Defender, Ansco, Hammer and Dupont (see Table 2.2) (Horvath 1987; Walsh 1995; Jamison 2003; Valverde 2005; Adelstein 2010; Eaton et al. 1985).

Despite the usefulness of this information, during this investigation far less information concerning timelines for film production in Europe was found. As previously mentioned in sections 2.1.3.1 and 2.2.3.1 there is still a gap to fill on this subject. As presented in Chapter 2 (see sections 2.1.3.1 and 2.2.3.1) information concerning CN's and CA's film-based negatives production was gathered during a visit to Agfa-Gevaert archive in Belgium. From the information gathered it was possible to contribute to this timeline.

Thus, based on the issues presented, dating information is not a conclusive basis for the identification of films. Additionally, not all manufacturers gave information about production periods. Furthermore, the use of films on dates after those reported in the literature can also prompt misidentifications. What follows is a breakdown and discussion of the pros and cons of the visual references of embossed edge printing terms and notch codes for the identification of film negatives.

3.2.2 Visual identification

On a routine basis, the identification of film materials can be supported by simple identification methods. Internal evidence as edge printing and notch codes are two visual references proposed for identification of film-based negatives. Producers provided this valuable information by embossing data onto the film's edge (Fischer 2012). The embossed data are references to the type of film base, producer's trademark, notch code and manufacturing code (Fischer & Robb 1993; Horvath 1987; Valverde 2005).

3.1.2.1. Edge printing

The fire hazards caused by CN films (Smither & Surowiec 2002; Ostroff 2010) led to the development of more stable supports, initially CA and later polyethylene terephthalate (PET) and polyethylene naphthalene (PEN) (Valverde 2005, 29). By embossing the words "*Nitrate*" or "*Safety*" into the films, manufacturers established a reference code for a straightforward identification of the film base. The designation "*Nitrate*" is given to CN films and "*Safety*" is correlated to CA films, assuring the non-flammable nature of the CA base (Valverde 2005, 22,24).

By implementing this methodology, the industry sets a timeline for the use of different film supports, being that "*Nitrate*" term was used specifically between the 1930s and 1950s (Valverde 2005), while since the 1930s until the 1990s, the embossing of the designation "*Safety*" for CA supports was implemented (Valverde 2005; Fischer & Robb 1993; Fischer 2012; Lavédrine 2008). However, the designation "*Safety*" was also used for polyester film bases (Valverde 2005, 30).

Additionally, it is important to highlight that edge printing identification was mostly performed on sheet films (Fischer & Robb 1993; Fischer 2012).

Examples of edge printing photographed during the framework of this study are presented in Fig. 3.3.

Figure 3.3 Edge printings for cellulose nitrate ("Nitrate") and cellulose acetate ("Safety") film based negatives (top). An example of a reversal film (duplication) with a reference to the type of photographic emulsion (panchromatic) (bottom). © Élia Roldão.

Despite the useful contribution for identifying film supports, edge printing may still not be conclusive. For instance, duplication[55] may lead to misinterpretations or inconclusive results due to the inevitable transference of marks from the original film to the reversal

[55] Duplication is a preservation strategy in film archives in which the films are copied or transferred to new photographic support (analogue photography).

film (Fig. 3.4, bottom image) (Fischer 2012; O'Connor 1999). Also, edge printing was not a common procedure for all manufacturers; therefore, there are film negatives with no reference to the type of support.

3.1.2.2. Notch codes

Notch code is the term used to describe small cuts made on the side of films by manufacturers (Fischer 2012). These cuts were used by photographers in the darkroom to identify the emulsion side when the code was on the upper right-hand corner of the film (Horvath 1987; Fischer 2012; Jamison 2003) (Fig. 3.4).
According to David Horvath[56] (1987), Fernanda Valverde (2005) and Monique Fischer[57] (2012), Kodak sheet films with a 'V' shaped notch code are pre-1949 negatives with a CN base (Fig. 3.4). However, O'Connor (1999) also mentioned that after 1949 Kodak used the aforementioned code to identify Safety film manufactured.

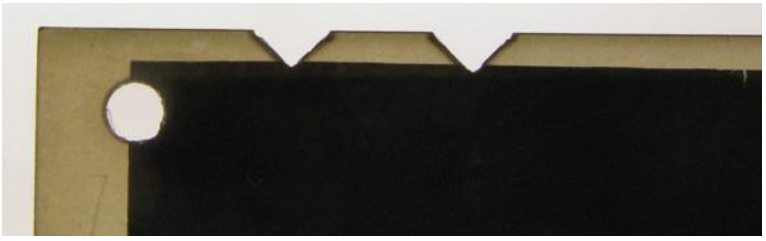


Figure 3.4 Example of a notch code from a plastic negative from the SIPA-DGPC collection. © Élia Roldão.

For CA film-based negatives, Fischer (2012), Valverde (2005) and Horvath (1987) pointed out the use of a 'U' shaped notch code by Kodak from 1925 to 1949. Additionally, Horvath mentions that in the same period Kodak also used a 'single square' notch code to identify CA-based films.
According to the technical description found in Photo-Lab-Index (1946, 1956), edited by Henry M. Lester[58] and Henry M. Lester and John S. Carrol, notch codes are correlated with photographic emulsions. Therefore, at the beginning, the relationship between notch code and photographic emulsion was a subject of relevance for photographers. However, currently, the correlation between those codes and film base are one of the bases for identification of film-based negatives used by archivists and conservators since these codes allow for fast and non-destructive identification. During the framework of this study, a survey of notch codes was gathered, which is presented in Appendix II. Some of the examples presented in Appendix II result from the efforts made overtime to compile

[56] Curator at the University of Louisville Photographic Archives. In the research carried out in 1987, Horvath gathered and published a wide list of notch codes employed by Kodak, Defender, Agfa/ANSCO and HAMMER (Horvath 1987, pp.52–70).
[57] Senior photograph conservator at the Northeast Document Conservation Centre, Andover, MA, U.S.A..
[58] Scientist and industrial photographer and a photographic publisher and inventor.

lists of notch codes and to correlate those with the type of films base (Appendix II, Fig.s II.1-II.3).
However, Bertrand Lavédrine[59] (2000) noticed the reuse of some of the notch codes for diverse types of film supports. Therefore, it may be concluded that the identification of film-based negatives based on these marks is subjective and may lead to misinterpretation.
Given the drawbacks presented, it is recommended using additional methods to ensure accurate identification of film supports.

3.3 Non-destructive tests

Excluding the accuracy and reliability of analytical methods (see section 3.2.3.), the costs associated with materials and solvents needed for identification and assessment of the film support are decisive factors for selecting tests.
In the field of conservation of photographic materials, it is common to resort to simple tests that demand no technical knowledge, allowing straightforward interpretation of the results. An effective and simple non-destructive test for plastic identification is the polarization test which is used to identify polyethylene terephthalate (PET) film supports (Fischer 2012,3). This is a simple and inexpensive test that allows a preliminary distinction between cellulose esters and PET films, an important task when considering the preservation of film collections (Walsh 1995). However, it does not allow the distinction between CN and CA film-based negatives, therefore, it is necessary to perform destructive tests to identify and assess film supports.

3.4. Destructive tests

The identification methods used in conservation were adapted from the plastics' industry (Shashoua 2008c; Coxon 1993). In this section, only tests recommended for the identification of cellulose ester film supports will be presented.
Commonly, destructive tests are used in a second level of identification whenever there are no visual codes (edge printing, notch codes and dating information) or when these codes lead to inconclusive results (Fischer 2012). The selection of simple destructive identification methods is often based on the lack of scientific equipment, but mostly on the straightforward interpretation of the results obtained (Coxon 1993; Shashoua 2008c; Lavédrine 2000).
Diphenylamine spot test, flotation test and burning test are common simple methods used by conservators (Fischer 2012; Lavédrine 2000). However, these are destructive, and can also lead to inconclusive results. Additionally, considering the existence of thousands of negatives stored in archives, these tests may be time-consuming.

[59] Director of the Centre de Recherche sur la Conservation at Paris, France. Lavédrine teaches conservation science, preventive conservation and preservation of audio-visual collections.

Despite the low costs associated with these types of tests, there are safety rules that should not be forgotten when using them. Due to the use of toxic solvents and acidic solutions, the lab must provide safety conditions for the person responsible in performing these tests (Fischer 2012; Eaton et al. 1985).

3.4.1. Diphenylamine spot test

The *diphenylamine spot test* is one of the field methods used for the identification of CN materials (Shashoua 2008c; Coxon 1993). It consists of observing the reaction of the material from a small droplet of solution (0.5% diphenylamine in 90% sulphuric acid in 10 mL of water) (Williams 1994)[60]. The formation of a deep blue colour is a positive indication of the presence of CN and the absence of colour indicates its absence as shown in Fig. 3.5 (Williams 1994; Lavédrine 2008; Fischer & Robb 1993; Coxon 1993).

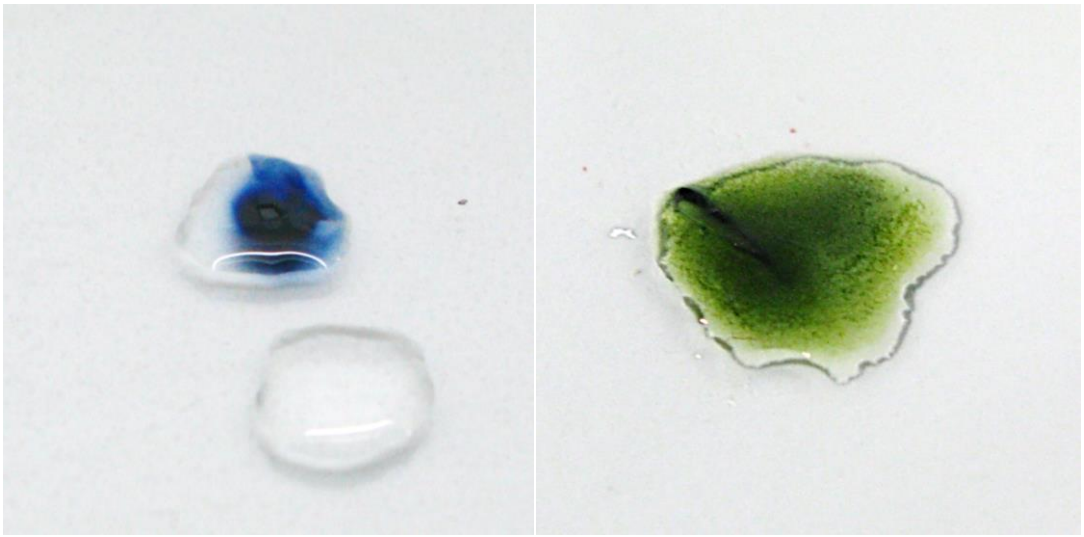


Figure 3.5 - Results obtained with diphenylamine spot test for the identification of CN film-based negatives. Left image: positive identification. Right image: negative result (absence of CN). © Élia Roldão.

The blue colour results from the oxidation of diphenylamine in sulfuric acid (Grebber & Karabinos 1952; Shashoua 2008c). Studies on the oxidation of diphenylamine in sulphuric acid using several aliphatic nitrocompounds suggests that the blue colour arises from the presence of benzidine (1) and phenazine (2) salts (Grebber & Karabinos 1952), (Fig. 3.5 and Fig. 3.6).

[60] Information about solution preparation according to a protocol proposed in the article "The Diphenylamine spot test for cellulose nitrate in museum objects – Canadian Conservation Institute (CCI) – Notes 17/2".

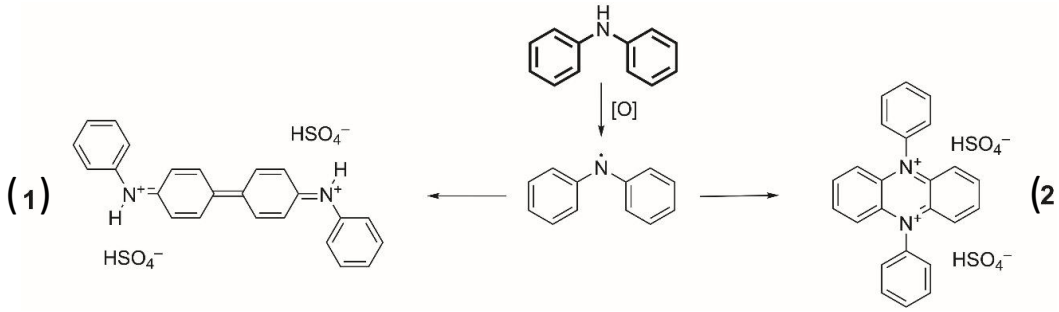


Figure 3.6 – Proposal of a full scheme for the blue colour formation in the diphenylamine test for nitrocompounds.

Similar reactions (interferences) may occur due to other strong oxidizing agents such as chromates, ferric salts and nitrites that can oxidize diphenylamine giving false results (Williams 1994; Roberts 1949).

Additionally, the possible presence of CN in the subbing layer of CA film-based negatives (Chapter 2, section 2.2.4) may also lead to an incorrect identification of the support by creating a "*very faint blue tinge*" (Fischer & Robb 1993; Fischer 2012; Coxon 1993). Lavédrine (2000) suggests the removal of the subbing layer in order to avoid interpretation errors.

According to Williams (1994), the formation of the colour's orange, green, yellow or brown are correlated with the absence of CN. Fig. 3.5 (right) shows the result of testing a CA-based negatives (film identification performed by infrared spectroscopy) with the diphenylamine test.

Furthermore, this test may be a health hazard due to its acid content. The conservator should gather all the laboratorial conditions to extract the toxic vapours released by the solution creating a safe environment when performing the test (Fischer 2012; Shashoua 2008c).

3.4.2. Density or flotation test

Density[61] or relative density (specific gravity), is one of the physical properties that may allow differentiating plastic materials (ASTM D792 2008). Density (ρ) is the ratio between mass (*M)* and volume (*V),* of a material (Flory 1953; Braun 2013):

$$\rho = \frac{M}{V}\ [g/cm^3]$$

This simple test requires only the placement of a sample in a test tube with a solvent or a mixture of solvents, depending on the type of polymer tested (Pavão 1997; Fischer 2012).

[61] Density relies on a known molecular weight and molecular structures of a specific plastic material in a known volume of a specific solvent (Shashoua 2008d; Braun 2013).

According to Braun (2013) and as described in the ASTM *Method B Testing Solid Plastics in Liquids Other Than Water*, selected liquids must not dissolve the sample otherwise the identification is compromised. Thus, the selection of solvent is based on the non-hygroscopic nature of the liquid and its specific gravity (SG) that must be inferior to the SG of the sample (Anon 2008). Eaton (1985), Fischer (2012) and Lavédrine (2000) endorse the use of trichloroethylene.

Table 3.1 shows the approximate densities for cellulose esters and solvents seldomly used for the density or flotation test indicated in the literature.

As presented in Table 3.2, film supports, and solvents have similar densities. According to the relative densities of CN and CA's polymers, it is expected that CN samples will sink, and CA samples will float near the surface whenever the test is performed with trichloroethylene (Eaton et al. 1985; Valverde 2005; Fischer 2012). Since both CN and CA polymers have low crystallinity, the results rely only on the density of those polymers (Table 3.1).

Table 3.1 Approximate densities for cellulose esters polymers and solvents seldomly used for the density or flotation test (Shashoua 2008c; Braun 2013; Brandrup et al. 1999; Pavão 1997; Neblette 1952, p.153)

	Density (g/cm^3) (References)					**Crystallinity (%)**
Solvents			**(Pavão 1997)**	**(Brandrup et al. 1999)**		
Trichloroethylene	____	____	1.47	1.46		_____
1,1,1 Trichloroethane	____	____	____	1.33		_____
Materials	**(Braun 2013)**	**(Shashoua 2008a)**	**(Pavão 1997)**	**(Wypych 2016)**	**(Neblette 1952)**	**(Shashoua 2008a)**
CN	1.34-1.40	1.35-1.40	1.50-1.53	1.35-1.40	1,5	Low/amorphous
CA	1.25-1.35	1.3	1.26-1.29	____	1.3	Low/amorphous
CAB	1.15-1.25	____	1.22-1.24	1.16-1.26	1.2	____
CAP	1.18-1.24	____	1.25-1.27	1.17-1.25	1.3	____
CTA					1.3	

Despite the significance and use of the density test, there are some factors that may alter the materials densities resulting in changes in the results. Loss of plasticizer, porosity, composition, heterogeneous degradation and local differences in crystallinity are pointed as some of those factors (Anon 2008). Thus, chemical and physical changes of the negatives base may lead to inaccurate results or misinterpretations (e.g., in opposition to what was described previously, when degraded CA base sinks) (Fischer 2012; Pavão 1997).

Such as diphenylamine spot test**,** this test raises safety issues related to the use of trichloroethylene, a volatile, toxic and carcinogenic solvent (Fischer 2012; Lavédrine 2000).

3.4.3. Burn or flame test

Several indicators of the flame test[62] can help to determine the type of polymer according to the colour of the flame, odour, speed of burning, vapour's pH and behaviour of the sample (if it melts or drips, if it self-extinguishes or continues to burn after being removed from the flame) (Shashoua 2008c). Table 3.2 shows the expected results for cellulose esters.

Table 3.2 Summary of several remarks to be considered when performing identification of CN, CA, CAB, CAP and PET film based negative through the burn or flame test (Shashoua 2008c; Eaton et al. 1985; Fischer 2012; Braun 2013)

Observations	**Materials**			
	CN	**CA**	**CAB**	**CAP**
Colour of the flame[63]	Bright white, yellow, burn explosively	Light green or yellow with sparks	Dark yellow with blue edges, slightly soft	Yellow
Odour	Camphor, nitrogen oxide	Vinegar, acetic acid	Rancid butter	Burn sugar
Speed of burning	Fast	Slow	Slow	Fast
pH	1.0-4.0	2.5	---	----
Remarks	Burns completely and vigorously	Black smoke with soot	Black smoke with soot	Smoke black smoke

Regarding the colour of the flame, yellow is the flame colour for all types of film supports. However, as described in Table 3.2, there are some subtleties correlated with each type of cellulose ester films.

The burning speed is also considered for identification. As expected, CN polymer samples burn vigorously, quickly and completely, while CA and CAB have a lower burning rate

[62] For a correct identification, the sample must be held vertically with metal tongs and ignited on its top (Fischer & Robb 1993; Eaton et al. 1985).

[63] In general, yellow, is the flame colour for all types of film supports (Table 3.2). However, Braun (2013, 30) described different tones for CN (white) and CA (green). Additionally, the colour of the flame edges is different for each type of polymer: blue edges may help to distinguish CAB from PET. Shashoua (2008c) also describes a flame with sparks for CA and mentions an explosive burning for CN.

when compared to CAP (Table 3.2). Dietrich Braun[64] (2013) alerts for the interference caused by flame retardants on the flammability of polymers and how those additives may lead to different outcomes from expected. During the test, pH may also be evaluated[65] (Shashoua 2008c; Braun 2013). According to data presented in Table 3.2, as expected the lowest pH is attributed to CN polymers. However, as is possible to see, the range of values is not exclusive since the value indicated for CA is in the range of values indicated for CN polymer. Furthermore, it is indicated that the odour of the flame is specific for each burned polymer and may provide the identification of the material (Table 3.2).
The identification of polymeric films based on these aspects is subjective since it requires extensive experience and baseline references to reach a correct assessment. As section 2.2.2.1. describes the changes in formulations over the years, such as the addition of flame retardants to CN films after 1930, can confound the results. Besides being a fire hazard when performed near other CN film-based negatives, this destructive test demands sizable samples (Fischer & Robb 1993), which may pose ethical obstacles for a photograph conservator when applied to historical materials (Fischer 2012; Eaton et al. 1985).

3.5 Degradation

Concerning the stability of photographic materials, Reilly [(2010)][66] said:

> *The complexity, variety, and extreme fragility of early photographic materials are often underestimated by archivists and collectors. Their stability problems have both technical and human dimension; to preserve them it is essential to know the objects and their problems, and to continually monitor how they are being handled and stored.* Reilly (2010)

According to Reilly (2010), the in-depth knowledge of photographic materials will allow assessing their decay. Therefore, degradation patterns can contribute to the identification and assessment of photographic materials (Eaton et al. 1985; Fischer 2012). Additionally, those parameters are the basis for visual assessment and for the establishment of preventive actions on film collections, such as rehousing, duplication, selection of enclosures and storage conditions and definition of treatment priorities (Lavédrine 2000; Fischer & Robb 1993).

[64] Leader of the German Institute for Synthetic Materials in Darmstadt (Deutsches Kunststoff-Institut (DKI)) until his retirement in 2000.
[65] The vapour's pH is measured by placing a polymer sample together with a moistened pH indicator strip inside a closed glass tube. A colour shift indicates the increasing acidic vapours. The evaluation is based on the pH ranges of values attributed for each colour.
[66] This text is part of a presentation made by James M. Reilly in the American Institute for Conservation annual meeting. The meeting took place was in 1980, in San Francisco.

3.5.1. Macro evaluation of degradation

As presented in Chapter 2, the degradation of cellulose ester films is complex. Nevertheless, throughout the history of negative film collections' preservation authors have proposed degradation charts with 5 to 6 conditions grades (Valverde 2005; Fischer 2012; Fischer & Robb 1993; Lavédrine 2000; Horvath 1987). Those charts result from a systematic gathering of degradation signs correlated to CN and CA film-based negatives. For this reason, the various degradation signs for CN and CA film-based negatives presented in the literature were gathered, studied and are summarised in Table 3.3. The degradation signs presented are related to the overall object or, in other words, with all layer's present in the photographic film.

Table 3.3 Compilation and description of CN and CA film-based negatives six degradation grade (Valverde 2005; Lavédrine 2000; Wilhelm & Brower 1993; Fischer 2012; Reilly 1993).

Film support	Degradation grade	References			
		(Valverde 2005)	(Lavédrine 2000)	(Wilhelm & Brower 1993)	(Fischer 2012)
Cellulose Nitrate	**1**	*No deterioration* *Legible image*	Discolouration of the base (*brownish yellow to dark brown*) Oxidation of the silver image (*silver mirroring*)	*Amber discoloration* and image fading	*No deterioration*
	2	Yellowing of the support and *silver mirroring* *Legible image*	Pronounce odour of nitric acid In humid environments the emulsion became tacky In dry environments the base became brittle	Sticky emulsions and films adhere to each other	Yellowing and mirroring
	3	Stickiness of the film and *strong odour of nitric acid* *Legible image*	Formation of gas bubbles in the base. A strong odour of nitric acid. Nitric acid release, probably attacking and catalysing the deterioration of objects stored nearby	Formation of gas bubbles and strong (*noxious*) nitric acid odour	Stickiness and *strong* (*noxious*) nitric acid odour
	4	Amber discolouration of the film and slight image fading *Partially legible image*	Image loss due to the stickiness of negatives that are stick among them or to enclosures	Film softens and sticks to each other films or stick to enclosures A *viscous froth* may cover the film	Amber discolouration of the base and image fading
	5	Softening of the film that sticks to other negatives or enclosure materials *No legible image*	A brownish powder resulting from the degradation of the polymer	*Brownish acrid powder*	Softening of the film that sticks to other negatives or enclosure materials
	6	*Brown acid powder*			*Brownish acid powder*

		(Valverde 2005)	(Lavédrine 2000)	(Horvath 1987)	(M. Fischer 2012)
Cellulose Acetate	**1**	*No deterioration* *Legible image*	*Slight odour of acetic acid* but in good condition	*No deterioration* *Flat negative*	*No deterioration*
	2	Shrinkage and brittleness of the negative Acetic acid odour *Legible image*	The increase of the odour of acetic acid (strong) but still considered in good condition	Minor *or moderate edge symmetrical* curling *on the two or four sides* of the negative. Emulsion and base become *smooth*	Curling Blue or pink discolouration
	3	Curling Blue or pink discolouration *Legible image*	Curling and slight brittleness of the base	Recognisable acetic or butyric acid odour	*Shrinkage and brittleness* Odour to acetic acid
	4	Warping *Legible image*	Bloom and weeping (migration of plasticisers) Warping	Warping	*Warping*
	5	Plasticisers migrate (weeping and crystal formation) *The image may or may not be legible*	Support is brittle Formation of wrinkles on the emulsion layer	Blistering and bloom	Blistering and bloom
	6	Channelling *The image may or may not be legible*		Crystal formation and delamination	*Channelling*

Through this data it is possible to visually assess the chemical and physical decay of each negative and oversee the evolution of the degradation grade. The main signs of degradation for cellulose ester film-based negatives are discolouration, silver oxidation (silver mirroring), brittleness, warping, blistering, shrinkage, channelling and delamination.

Besides these degradation signs, characteristic odours are correlated with the release of acidic products resulting from CN and CA chemical decay. Overall, it is possible to conclude that chemical and physical degradation signs progress in tandem from stage 1 to stage 6.

As shown in Table 3.3, a general agreement is seen in the description of the degradation signs, being possible to correlate those signs with condition grades. However, a difference is seen in what each author considers to be the starting point. While some authors established that film negatives do not have degradation signs in stage 1, others have an opposite point of view indicating that at that stage film-based negatives already have degradation signs. Therefore, this issue points out to a certain subjectivity or difference in the professional practice that may reflect on the assessment criteria currently used in film archives. It is believed that the differences found between authors, in respect to descriptions and establishment of degradation grades, are supported by the relevancy that each author attributes to degradation patterns which he believes to be fundamental markers for macro assessment. By comparing the authors' descriptions for levels 2 to 4 of degradation, it is possible to conclude that minor changes in the intensity of the degradation signs may lead to variations in the final conclusions.

Discolouration and odour are transversally considered degradation markers for cellulose ester films. While for CN film-based negatives yellowing, amber and brown hues are correlated with film base decay (Eaton et al. 1985, 89-93), the formation of blue or pink hues is correlated with CA film-based negatives (Reilly 1993; Lavédrine 2000). Additionally, green or magenta hues are also correlated with the decay of film-based negatives (Jamison 2003, 5). The hues correlated with CA film decay result from a reaction of the anti-halation dyes with the acetic acid released during the support deterioration reaction (Reilly 1993; Lavédrine 2000). Horvath (1987), Reilly (1993) and Valverde (2005) suggest that it is possible to identify the type of film support and manufacturer based on the colour rendered during the degradation of CA film-based negatives, in that a pink hue would indicate a Kodak film and a blue hue Agfa and Ansco.

Concerning CN film-based negatives stickiness, blistering, increasing nitric acid odour, film softening, and loss of emulsion layer are pointed out as common degradation signs that allow assessing the condition of the support as well as of the emulsion layer (Table 3.3). In addition, the release of nitric acid from that reaction promotes the oxidation and fading of the silver image (Table 3.3). Concerning CA negatives, *vinegar syndrome*, shrinkage, brittleness, channelling, and delamination are degradation signs that indicate chemical and physical decay of the base. Blistering and plasticizers exudations on the surface of the negatives are also very common signs of degradation of CA supports

(Table 3.3). Blisterig is also common on both CN and CA polymers indicating the formation of gases trapped in the bulk of CN polymer (Lavédrine 2000; Wilhelm & Brower 1993). For cellulose acetate-based negatives, blistering is associated with CN adhesive subbing layer (J. Orraca 2010) and the migration of plasticizers (Valverde 2005; Fischer 2012; Horvath 1987).

As already said, the release of acidic odours is a result of CN and CA polymers decay (Quye & Keneghan 1999; Shashoua 2008d; Quye et al. 2011; Reilly 1993; Lavédrine 2000). The odour occurrence constitutes a warning indicator for film decay and for risks of catalysing the degradation of the overall film collection and other materials in the surrounding environment (Table 3.4) (Valverde 2005; Lavédrine 2000; Fischer & Robb 1993; Reilly 1993).

Regarding the degradation patterns described by several authors, which are summarized on Table 3.3, some issues deserve further attention. The absence of degradation and the similarities between the degradation patterns of CN and CA bases may lead to misinterpretations.

3.5.2. Physical methods for identification and evaluation of the degradation grade

Film decay is manifested by significant changes in physical properties. Warping, shrinkage or loss of dimensional stability are some of the most common signs of degradation. Curling is most frequent in film supports, which do not have an anti-curling layer.

3.5.2.1 Dimensional analysis

Still photography, motion picture film and sound film supports were commercially available in different standardised formats (Valverde 2005; O'Connor 1999). The most common film-based negative formats were the 16mm, 35mm, 120mm, 4x5 inches, 9x12 cm, 10x15 cm, 13x18 cm, 15x20 cm and 18x24 cm.

Film shrinkage is a consequence of the loss of plasticizers and denitration or deacetylation of the CN and CA polymers, respectively (Read & Meyer 2000; Valverde 2005; Bigourdan 2000). According to the International Organization for Standardization (ISO) normative reference ISO 18903:2001 for determining dimensional changes, it is possible to have a quantitative evaluation of shrinkage of a film by measuring the general dimensions of processed and aged film-based negatives and comparing it with a standard measure of a specific format.This is a straightforward and non-destructive method that allows evaluating the loss of physical properties in the negatives. However, it may be time-consuming when considering the vast quantities of film-based negatives present in archives.

2.5.2.2 Edge perforation

Edge perforation allows for a quantitative evaluation of the shrinkage of motion picture film supports (Read & Meyer 2000). A pristine polyester strip of the film without an image is used to compare with a historic film. The perforations are aligned and if they don't match precisely it indicates film decay by shrinkage. If possible, this evaluation is performed at a minimum of 100 frames, conveniently identifying percentage levels of shrinkage. If the mismatch is recorded in the first frames, it denotes that the film is severely degraded. If it occurs at the 100-frame mark, then it's an indication of an earlier stage of decay. A 1% shrinkage corresponds to an out register of one whole frame (Johansen 2004; Read & Meyer 2000).
For motion picture film archives measuring shrinkage is important to evaluate the extent of the film support decay but also to establish prevention and duplication priorities (Johansen 2004; Read & Meyer 2000).

2.5.2.3 Curling

Curling is the term used to describe the tendency of some film-based negatives to roll, particularly when exposed to high relative humidity. Curling is frequently related to the absence of the anti-curling layer on the back of the support of early cellulose nitrate film-based negatives manufactured before 1903 (Valverde 2005). The moisture absorption rate of the film base is lower than that of the emulsion layer, resulting in the curling of the film.
After 1903, an anti-curling layer was applied to all film-based negatives to counteract the tension caused by the emulsion layer and to promote dimensional stability (Valverde 2005, Jamison 2003, 5). Planar tensions are the result of the hygroscopic nature of the gelatin present in the photographic emulsion.
The observation and evaluation of film negatives curling is a simple method that allows identifying early cellulose nitrate film-based negatives (Valverde 2005). However, curling may also result from the chemical and physical decay in CA films (Lopes 2014; Johansen 2004). Therefore, it is imperative to accurately identify the film base to avoid misinterpretations.

3.6.3 Chemical methods for identification and assessment of the degradation grade

The preservation and conservation of film-based negatives require methods to carry out qualitative and quantitative evaluations of deterioration. With the aim to minimize the risks of acidic vapours affecting entire collections, the early detection of degradation products such as acetic acid (CH_3COOH), nitrogen dioxide (NO_2) and nitric acid (HNO_3) are key aspects of film preservation (Adelstein et al. 1995; Curran et al. 2014).

Colourimetric methods of detection and monitoring acidic vapour release from works of art have been proposed (Grzywacz 2006; Matsumura et al. 2002; Hackney 2016). Fischer & Reilly (1995) and Valverde (1997) focused their work on developing indicators for acidic vapour release in CA and CN films, respectively. Strlič (2004) and Tsé (2007) compared potentiometric methods and pH testing devices on works of art. Potentiometric and colourimetric methods were used by Edge et al. (1989; 1990) and Adelstein et al. (1992a; 1995a; 1995b), specifically concerning the quantitative evaluation of acidification of cellulose ester photographic negatives and motion picture films.
This section will focus on, colourimetric methods used for detection of acetic acid, nitrogen dioxide and nitric acid, as well as on potentiometric methods used to measure the acidity of cellulose ester films.

3.6.3.1 Colorimetric methods for assessment of cellulose nitrate and cellulose acetate film-based negatives

Acid-base indicators used to assess the pH of works of art rely on the sensitivity of specific organic dyes to changes in H^+ concentration that will result in different colour renderings (Tse 2007). The results are an estimation of the pH since this method does not allow for an exact value but rather intervals of values. The capability of semi-quantification relies on the dyes' reaction and also on moisture (the lack of moisture will preclude the necessary chemical reactions) (Shashoua 2008a).
The two colourimetric methods used for evaluating off-gassing of CN and CA film-based negatives are pH indicator solutions and pH paper strips (Adelstein et al. 1992a; Fischer & Reilly 1995).
The universal pH indicators are made by combining solutions of several compounds that allow detecting pH in a range of 1 to 14. This type of paper strip indicator has to be moistened before performing the measurement (Shashoua 2008a), which is a disadvantage since it might stain the object being tested (Tse 2007).
The use of pH indicator strips was established to oversee the release of acidic gases from CN and CA artefacts since it is a non-destructive method with moderate cost (Matsumura et al. 2002; Shashoua 2008a; Fenn 1995). The most commonly used monitors used in the field of conservation and preservation of artworks are selected according to cost, testing times and straightforward interpretation of the results (Fenn 1995).
The following paragraphs will focus on the most common indicators used in the field of conservation and preservation of cultural heritage, in particular of CN and CA artefacts, film-based negatives and movie picture film archives.

With the aim of detecting nitrogen oxides (NO_x), sulfonephthalein dyes have been used as indicators (Shashoua 2008a; Shashoua 1999; Matsumura et al. 2002). These indicators

came as an alternative to the *Oddy test*[67](Grzywacz 2006; Hatchfield 2004). However, the *Oddy test* requires is destructive (requires sample collection).

Cresol red (o-cresolsulfonephthalein)[68] and cresol purple (m-cresolsulfonephthalein)[69] dyes are used to detect NO_x resulting from CN polymer decay (Matsumura et al. 2002; Shashoua 2008a; Hatchfield 2004). For more details about the cresol red and cresol purple see Appendix III.

Table 3.4 was designed for this study with the aim of presenting data correlation between distinctive colours registered and pH with dye embedded in paper strips exposed to NO_x.

Table 3.4 – Comparative colour and pH range for dyes used to develop paper indicators tailored for evaluation of release of NO_x

Dyes					Reference
Cresol red	Colour range	Pink orange	Yellow	Reddish/purple	(Hatchfield 2004)
	pH range	0.2	1.8	8.8	
	Colour range	Red-orange	Yellow	Violet	(Matsumura et al. 2002)
	pH range	0-1.8	2.0-7.0	7.0-8.8	
	Colour range	Orange	Yellow	Reddish purple	(Fenn 1995; Shashoua 2008a)
	pH range	0.2-1.8	1.8	8.8	
	Colour range	Bright yellow	Orange	Red	(Harthan et al. 1997)
	pH range	3.5	4.4	5.5	
Cresol purple	Colour range	Red	Yellow	Purple	(Fenn 1995; Shashoua 2008a; Hatchfield 2004)
	pH range	1.2 – 2.8	2.8 – 7.4	7.4 - 9.0	
Alizarin red	Colour range	Colourless ←		Red	(Valverde 1997; Read & Meyer 2000)
	pH range		4.6-6.0		

Concerning cresol red, according to the literature and as shown Table 3.4, there is not a full agreement on the colour range.

Comparing the detection limits of cresol red and cresol purple it is possible to conclude that the latter has a higher detection limit (pH 1.2, 2.8 and 9). Nevertheless, both are

[67] The *Oddy test* was developed by Andrew Oddy, a former worker of the British Museum. The test was created to detect harmful volatile compounds, such as nitrogen oxides resulting from CN objects decay, in storage and display materials. Three metal (silver, copper and lead) coupons are used for detection (Thickett & Lee 2004).

[68] The *cresol test for nitrogen dioxide* consists of impregnating strips of unbuffered filter paper with solutions of the mentioned indicators in water or alcohol, in low concentrations (0.04% or 0.005% respectively - Hatchfield 2004; Fenn 1995; Matsumura et al. 2002).

[69] The cresol red and cresol purple (reagents) are prepared in a 0.04% (w/v) aqueous solution or in a 0.005% (w/v) alcohol solution (methanol or ethanol with 10% methanol). The acid dyes are alcohol soluble and the mono-sodium salt is water soluble (Matsumura et al. 2002).

suitable for detecting NO_x and to identify and distinguish between CN and CA objects (Fenn 1995).
According to Julia Fenn[70] (1995), regarding the efficiency of these indicators, there are several aspects to be considered. One is the interference caused by low temperatures in the detection of pH changes, especially with commercial pH indicators. Therefore, humectants such as glycerin are used to improve the performance of the testing materials (Shashoua 2008c). However, the development of nitroglycerin may occur when the indicator is put in contact with an object releasing nitrogen dioxide (Fenn 1995).
Despite the drawbacks, present sulfonephthalein indicators proved to be a simple and useful to assess the decay of CN materials, and also financially accessible (Fenn 1995).

The use of anthraquinone dyes (e.g. alizarin red[71]) for the development of indicators with which the assessment of CN films could be performed was investigated (Valverde,1997). The results are based on dye fading caused by the reaction with the increasing development and releasing of nitrous and nitric acids by the CN support, supporting the assessment of the film condition (Table 3.4) (Valverde 1997; Read & Meyer 2000; Adelstein et al. 1995b). Despite the effectiveness of the results shown, it is important to keep in mind that this test is destructive, as it requires samples of the material being tested.
Concerning cellulose acetate-based negatives, the *vinegar syndrome* denomination is used to characterize the emission of acetic acid (CH_3COOH) resulting from the chemical decay of those materials (Lavédrine 2000). Although acetic acid is weak acid (AcOH, pK_a = 4.76), early detection of it allows detecting the condition grade of the film-based negative and hence prevents contamination of adjacent film material (Adelstein et al. 1995b). With the aim of establishing preventive measures to safeguard CA film collections, three commercially available indicators are suggested in the literature: Film Decay Detector Sensor® (FDD), DANEYE/Dancheck® and A-D (acid-detection) strips (Fischer & Reilly 1995; Reilly 1993; Hackney 2016).
Bromocresol green is identified as the indicator present in Danchek®[72] and Film Decay Detector Sensor® (FDD), both are respectively applied to a paper strip or dispersed in silica gel (Fischer & Reilly 1995; Shashoua 2008a). Both, FDD and Danchek®, were specially developed for long-term monitoring of motion picture film (Fischer & Reilly 1995). A similar products, Acid-Detection (A-D) strips, was developed by IPI[73] .Monique Fischer and James M. Reilly (1995, 14) launched a research to develop such indicators to

[70] Senior Conservator, Ethnography at Royal Ontario Museum (ROM).
[71] For more details about alizarin red dye see Appendix III.
[72] According to information available on the Dancan Cinema Services ApS website there are two commercial products available to detect vinegar syndrome: the Danchek AD strips and the Acid Detection Control Eye **(**DANEYE). The Danchek AD strips have paper substrate and the DANEYE with a silica substrate.
[73] Image Permanence Institute (IPI), a North American research centre, headquartered in Rochester, New York, actively collects, develops, and disseminates knowledge about the material nature of photographs in the 19th, 20th and 21st centuries.

test the efficiency of bromocresol green, bromothymol blue, chlorophenol red, m-cresol purple and methyl red dyes in detecting acetic acid.

Bromocresol green[74] provided the most satisfactory results, with a clear colour shift and higher saturation when prepared with alcohol (Fischer & Reilly 1995). To increase the pH range, 0.1N NaOH was added resulting in an increased range of colour change from blue to green to yellow (Adelstein et al. 1995a; Fischer & Reilly 1995).

As presented in the *User's Guide for AD-STRIPS - Film Base Deterioration Detectors*[75] (2001) a colourimetric semi-quantitative scale allows detecting and evaluating the increase of free acid[76]. The protonation of bromocresol green results in the gradual colour transition from blue (no acidity) to green, yellow and light yellow according to the acid vapours concentrations (see Appendix III).

In Table 3.5, a comparative summary of pH range, colour range, pH value and remarks for IPI and Danchek AD-Strips is presented. As much as possible, the AD-strips colours given in Image Permanence Institute (IPI)[77]and Dancan[78] webpages.

Table 3.5 IPI and Dancheck AD-Strips information summary of free-acidity levels, colours, pH values, odour and remarks on degradation (Reilly 1993; Jacobsen n.d.).

IPI A-D Strip		**Danchek AD-Strips**		
Free acidity level and colour	Remarks on degradation	Level and colour	pH and odour	Remarks on degradation
0	Good - No deterioration	0	6.0 none	Fresh film
		0	5.5 none	Degradation beginning
		0	5.0 none	Degradation is increasing
1	Fair to Good (deterioration starting)	1	4.8 weak	Degradation is increasing
1.5	**Autocatalytic point** (rapid decay)	2	4.6 Strong smell	**Autocatalytic** point Film should start to be monitored
2	Poor (actively degrading)			
3	Critical decay	3	4.4 Strong smell	The film should be duplicated
		3	<4.0 Strong smell	Urgent duplication

[74] For more details about Bromocresol green see Appendix III.

[75] User Guide of the AD-Strips provided by the supplier in which testing, and maintenance guidelines are given.

[76] Free acidity is the portion of the total acidity that exists in the form of acid in the film base and is related to the quantity of alkali required to neutralize the acid (Reilly 1993). According to Reilly (1993) the method used to measure free acidity is presented in ANSI Standard IT9.1-1992.

[77] The colour reference information presented for the A-D STRIPS is available on IPI's website https://www.imagepermanenceinstitute.org/imaging/ad-strips (accessed March 13, 2017).

[78] Full access to product details and colour reference is given in the website http://dancan.dk/?page_id=1807 (accessed March 13, 2017).

A shift in colours on the strips may not be in agreement with the scale provided by the suppliers since an *infinite number of steps* may result in several colour changes. Therefore, it is asked to the reader not to fix their attention on the colours presented in Table 3.5 but on the correlation given between free-acidity scale and pH values.
Overall, data shown in Table 3.5 allow concluding that gradual changes from blue, green to yellow correspond to an increase of the free acidity (from 0 to 3) and a decrease in pH (6.0 to below 4).
These products have shown to be extremely useful to assess CA film-based materials and support the establishment of priority actions for conservation and preservation of film collections (Fischer & Reilly 1995; Reilly 1993). Thus, no recommendations are given for film-based negatives at levels 0 and 1 (induction period). As presented in Table 3.5, the autocatalytic point is noticed at IPI AD Strip level 1.5 (free acidity 0.5) and Dancheck AD-strips level 2 (pH 4.6). At this stage of material deterioration, immediate action is required for the safeguard of the film itself and to prevent the contamination of film materials stored nearby that may not have undergone the same level of deterioration.
User's Guide for A-D Strips provides important and useful recommendations for the testing procedure. As described in the *User's Guide* the exposure time will depend on temperature, relative humidity and the acid concentration. The exposure time expected for an area at room temperature and 30-50% RH is 24 hours, whereas when testing an area at 2°C it may require an exposure time of up to 4 weeks. Reinforcing the dependence of humidity[79] Shashoua (2008a) refers that the strips may have a humectant (glycerol) to maintain the required moisture for the strips to react to acidic gases.
The effects of light on the indicators are highlighted by Hatchfield (2004), Shashoua (2008a). The authors mention the possible occurrence of interferences due to the sensitive nature of the dye to the light, recommending the test to be performed in dark closed enclosures.
Furthermore, the A-D Strips manual states that Bromocresol green sodium salt is soluble in water and alcohol, therefore, it is recommended to avoid the strips from coming in contact with the solvents. Additionally, the contact with plasticizers exudations (oily contamination) may also interfere with the results (Hatchfield 2004; Shashoua 2008a). Furthermore, a closed environment avoids the interference of other acidic pollutants present in an open environment (Hatchfield 2004; Shashoua 2008a; Reilly 1993).

Besides the aforementioned investigations, Matsumura, *et al.* (2002) studied the possible alternative indicators congo red, methyl orange and cochineal dyes for monitoring the emissions of CA costume accessories. The pH range of these dyes allows detecting not only acetic acid, but also other weak acids that may be present in storage room environments, thus reaching inconclusive results. Adelstein et. al (1995a) tested the use of bromothymol blue, chlorophenol red, m-cresol purple and methyl red reporting that all the dyes tested were *too sensitive*, resulting in fast colour shifts even for 'fresh films'.

[79] In the absence of humidity there will be no reactions between the bromocresol and the acidic vapours.

From the research, bromocresol green (also tested) proved to be the most reliable indicator to monitor CA film-based negatives and motion picture films. Therefore, bromocresol green has been consensually used to monitor CA film-collections and artefacts (Shashoua 2008).
Cresol red (*Sulfonephthalein indicator*) was also used as an indicator to monitor the emission of acetic acid from CTA film-based negatives (Harthan et al. 1997). The goal of the research conducted at the Manchester Metropolitan University was to find a non-destructive method in which cresol red was adsorbed onto a solid substrate with the aim to develop a long-term monitor to follow the decay of CA films.
The procedure to obtain a sensor system is described by Harthan (Harthan et al. 1997) where a paper substrate option was abandoned, and the adsorbents XAD-7 amberlite polymeric resin, silica gel and zeolite were tested. The adsorbent XAD-7 was selected because when compared with the other adsorbents tested it resulted in a higher pH range and it differentiated colours according to acetic acid emissions. To compare the results obtained with the sensors, pH potentiometric measurements were performed. Although these were clear advantages, some drawbacks were found. One is related to the colour change from red to dark pink, in an unexpected alkaline film. These results may have been caused by biological contamination, possibly residues of a cleaning agent (1,1,1–trichloroethane) or from film processing development agents, like sodium sulphite (Harthan et al. 1997).
There were also some discrepancies concerning the testing time and pH values that were obtained. According to Harthan et al. (1997), the results achieved gave the concentration of acid inside the can rather than assessing specifically the film pH. Although the results do not indicate the pH of the negative, they still are relevant since the data report the formation and concentration of gases that promote film degradation.
Additionally, plasticizers reacted with the indicator leading to a *feathery appearance*. Harthan *et al.* (1997) also highlight the possible instability of polymeric resins in certain pH ranges.
In spite of these drawbacks, the work developed by Harthan *et al*. (1997) opened new perspectives for monitoring film collections.

3.6.3.2 Titration method

The *titration method* has been used to assess the degradation of CN and CA films by measuring the increase in acidity (Adelstein et al. 1995a; Johansen 2004). Adelstein *et al.* (1995a) reported the first method implemented by which polymers were dissolved in organic solvents. The authors report the use of a mixture of methylene chloride-ethyl alcohol to dissolve CA films, and the use of two solvent mixtures, acetone-methanol or acetone or acetone-alcohol to dissolve CN films. The solution was then titrated with 0.1N sodium hydroxide (NaOH) and an indicator (metacresol purple). This titration method using the dissolution of the samples in organic solvents has several disadvantages. The

need to prepare the samples is time-consuming and the toxicity of the solvents and consequent health hazard are important drawbacks. Furthermore, the changes in the solubility of degraded samples result in a lack of reproducibility for severely degraded negatives (Adelstein et al. 1995a).

Additionally, the test for CN films was unsatisfactory due to the reaction of the solution with the indicator (bromothymol blue) or with the sodium hydroxide (NaOH) used (Adelstein *et al*. 1995a). Information about the dyes used as indicators is presented in Table IV.1 (see Appendix III) designed during the framework of this study.

Given these drawbacks, the water-leach free acidity test was developed. In this test, the organic solvents were replaced with water. This test consists on leaching the acidity of small samples (1 gram of material to be tested) in water (100 mL). It was concluded that the reliability of the results depended on the water temperature, leaching time and agitation. The authors found that the leaching water should be at 38°C, with constant stirring for 24 hours (Adelstein *et al*. 1995a). The second step of the test consists of titrating the solution with 0.1N NaOH[80](Adelstein *et al*. 1995a; Johansen 2004). The amount of NaOH expresses the value of the acidity needed to neutralize the acid that was leached by the water.

The substitution of the organic solvents in the first inception of the test with water allowed establishing a new method to assess the chemical decay of films without health hazards. However, this is still a destructive method and comparatively more time consuming than indicator paper strip tests.

3.6.3.3 Potentiometric methods used to measure acidity

Potentiometers have been employed to assess CN and CA film acidity (Allen *et al*. 1987; Adelstein *et al*. 1995a) namely using the *aqueous extraction method* (Edge et al. 1989; Edge, N. S. Allen, et al. 1990; Adelstein et al. 1995a; Harthan et al. 1997).

The method consists of immersing a film sample in distilled water for a variable testing time and temperature conditions (Edge et al. 1989; Adelstein et al. 1995a; Harthan et al. 1997.

Edge *et. al* (1989) and Harthan *et. al* (1997) immersed samples for 3 hours at room temperature; while Adelstein *et. al* (1995a) used different conditions and described that samples must be immersed in water at 38°C for 24 hours with constant stirring. Additionally, Adelstein *et. al* (1995a) tested an alternative method by soaking 1foot length of motion picture film in water. Several soaking times and temperatures were tested, and it was found that the most satisfactory results were achieved by soaking the samples for 2 hours in water at 21ºC. However, this method induces severe curling on the films.

[80] According to Johansen (2004), the test procedure is presented in ISO 18901:2000.

Although providing an accurate reading on acidity, the aqueous extraction method is destructive (Adelstein et al. 1995a) and relies on the quality of the water used in the test (Tse 2007) that should be distilled or deionized.

3.7 Analytical techniques used to identify and assess photographic and motion picture cellulose ester films

As presented in section 3.3.1, the identification of plastic supports is often related to visual degradation signs of each type of film base. Aside from the methods previously presented, there are relevant research works that have established forms of identification of supports and to characterize the role of intrinsic and extrinsic factors on the chemical and physical decay of films. Most of the investigations aim to predict the lifespan of film negatives and motion picture film and determine the most adequate storage conditions to preserve these materials (Allen et al. 1989; Edge et al. 1992). Several analytical techniques have been used to identify and assess the film base and coating layers (photographic emulsion and anti-curling layer). A summary of the research performed will now be presented.

The physical decay of still photography and motion picture films has always been a concern. In photography, with particular relevance for aerial film, dimensional stability is a major concern (Edge & Allen 1992). Also, for movie picture film, shrinkage may lead to the impossibility of projection or even photo-reproduction (Read & Meyer 2000). The assessment of the physical decay of negatives and movie picture films with different cellulose ester supports was studied (Adelstein *et al.* 1992a; Edge & Allen 1992). The tensile properties were assessed by measuring the tensile stress yield, tensile strength and elongation (strain) at break, modulus and toughness (Adelstein *et al.* 1992a).

Polymer degradation mechanisms were a key focus of several research works (Edge, *et al.* 1990; Adelstein *et al*. 1992a).

Nuclear magnetic resonance (NMR) spectroscopy was used to obtain qualitative and quantitative data regarding chemical and structural information to understand the degradation process of CTA motion picture film (Edge *et al.* 1992; Williamson 1994). The thermal and oxidative decomposition process, as well as crystallinity and transition glass temperature of CA, was also studied by performing thermal analysis, specifically differential scanning calorimetry (DSC) and thermogravimetry (Edge *et al.* 1992).

Allen *et al.* (1987) applied UV absorption spectroscopy analysis to monitor the degradation of CTA movie picture film, evaluating the carbonyl absorption region at 210 nm. The carbonyl formation resulting in CN films' decay was also monitored through UV-vis spectrometry (Edge, N. S. Allen, et al. 1990). Besides the carbonyl region at 285 nm, the decrease of nitrate groups was traced at 248 nm (Edge, *et al.* 1990).

Viscosity is one of the properties in which the assessment of the film base is supported on (Adelstein et al. 1992a; Edge et al. 1989; Valverde 1997). By measuring viscosity, it is possible to calculate the degree of chain scission or loss of molecular weight of the

polymer, results that support to assess the loss of chemical and physical properties (Adelstein et al. 1992a). The chain scission can be assessed by viscometry (Allen et al. 1987; Edge, N. S. Allen, et al. 1990; Edge, N. Allen, et al. 1990) and by measuring the percentage of insolubility (Edge *et al*. 1988).

Infrared spectroscopy of film was performed with the aim of evaluating the deacetylation or denitration and chain-scission of film supports. Two sampling methods for IR analysis are described in the literature: the cast film method (Walsh 1995) and the microtome method (Edge et al. 1989). Both approaches are destructive and time-consuming since they require removing the gelatine. Additionally, sample thickness and insolubility in later stages of degradation hinder IR spectroscopic analysis (Allen *et al*. 1987).

With the aim of performing a non-destructive analysis of film supports, Walsh (1995) and Johansen (2004) applied Attenuated total reflectance-Fourier-transform infrared spectroscopy (ATR-FTIR) directly to films. Walsh (1995) obtained accurate results for films without an anti-curling layers, such as CN motion picture films. However, the drawback posed by the presence of anti-curl layer resulted on the identification of the gelatine layer rather than the base once the ATR-FTIR beam penetrates only at the surface of the objects (few micrometres). To an accurate identification and characterization of still photography film supports is necessary to remove the gelatine layer. Furthermore, the author also tested the cast film method for which it is necessary to remove the gelatine layers and solubilize the samples, and found solubility problems for CA degraded samples (Walsh 1995).

Johansen (2004) also used ATR-FTIR to assess CTA film support degradation, following the decrease of carbonyl groups (C=O) and an increase of hydroxyl groups (O-H), aiming to correlate the IR data with the acidification results that were obtained with the *water leach* test and shrinkage measurements.

Fernanda Valverde (1997) performed IR analysis of CN films, in transmission mode, searching for a correlation between the chemical decomposition of the film and the increase in acidity and reported on the low sensitivity of this specific tool to detect chemical changes during the induction period.

Regardless of the destructive and time-consuming nature of IR spectroscopy, the research performed by the referred authors represents an enormous contribution to the conservation and preservation of films by identifying the tools that allow for an accurate identification and assessment of the supports.

For the identification of X-ray film, Konstatinidou *et al.* (2016) used organic elemental analysis (OEA) to distinguish CN from CA films based on nitrogen content. Data quantification considered the emulsion of nitrogen content as well as that of the film support. According to the results and discussion reported by the authors, OEA provides a quick and accurate identification of CN X-ray films. This destructive technique does not require sample preparation (the specimen minimum is 0.2mg).

Besides the analysis performed specifically of film bases, the role of coating layers, additives and processing solutions was also studied in depth. The possible contribution

of the emulsion layer on the stability or degradation of the film base was evaluated by measuring moisture gain through microwave spectroscopy (Allen *et al.* 1987; Edge *et al.* 1988). According to the authors, microwave spectroscopy is an extremely sensitive and non-destructive technique that allowed obtaining accurate results.

As previously said, additives such as plasticizers are considered one of the intrinsic factors that could contribute to film decay. Shinagawa *et al.* (1992) using nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC or GPC)[81] concluded that the plasticizer triphenyl phosphate (TPP) induces degradation of CTA films. More recently, McGath (2012) researched this by analysing CTA film plasticized with TPP with Raman spectroscopy.

The emission of acidic vapours resulting from the decay of the polymer was also subject to investigation (Glastrup 1995; Ballany 2000). Glastrup (1995) evaluated the decay of CA films based on the emission of acetic acid and phenol by Solid Phase Micro Extraction gas chromatography (SPME-GC) analysis. The results were obtained during artificial ageing of CA films treated with different types of fixers. The two most acidic gases found were acetic acid and phenol. Moreover, the author points to a correlation between the concentration of acid fixer and an increase of acidity. Furthermore, it was concluded that the increasing concentration of acid fixer leads to an increasing concentration of phenol and to the degradation of TPP plasticizer (Glastrup 1995).

With the aim of assessing the degradation of CA motion picture film, Ballany (2000) applied headspace gas chromatography (HS - GC) analysis to evaluate the surrounding atmosphere of artificially aged CA samples. Besides this particular work on CA films, the use of this technique has been reported on for assessment of CA and CN artworks (Curran et al. 2015; B. Lavédrine, A. Fournier 2012). Lattuati-Derieux *et al.* (2013) research presented relevant data concerning the assessment of plastics with headspace solid phase microextraction-gas chromatography coupled with mass spectrometry (HS-SPME-GC/MS). This non-invasive technique allowed identifying and establishing volatile markers based on the volatile organic compound (VOCs), additives, degradation products and monomer residues. The collected data allowed to create a survey based on the emission signature obtained for each plastic typology analysed. The results reported by Lattuati-Derieux et al. (2013) are valuable to preserve and monitor film negatives as shown by the analysis results of a CN object, where the technique identified camphene, fenchone, camphor and borneol isomers.

With the aim of performing straightforward and non-destructive identification of plastic artworks, near-infrared (NIR) spectroscopy, NIR chemical imaging (Šuštar *et al.* 2014), portable FTIR reflectance spectroscopy (Saviello et al. 2016) and Total Reflectance Fourier Transform Infrared (TRFTIR) spectroscopy (Cucci et al. 2013) have been successfully applied. Although positive results have been obtained, the gelatine coatings present on plastic negatives (Chapter 2) challenged identification through these methods (Konstantinidou et al. 2016).

[81] Size exclusion chromatography was formerly known as gel permeation chromatography (GPC)

Identification of photographic and cinematic films still demands further investigation to establish a straightforward, reliable and non-destructive tool that will support the preservation of film collections.

3. 8. Concluding Remarks

Several lists of notch codes and preservation guidelines with simple chemical tests and visual references for identification and assessment of the films have been published. Those publications are most helpful for archivists, librarians, conservators and other caretakers responsible for the preservation of film collections; however, they do not clarify all the issues that concern the broad range of cellulose ester film supports.

Information provided by the manufacturers (dating information, edge printing and notch codes) may be inconclusive or led to misinterpretation. Dating information helps to establish the type of cellulose ester films present in the collections by crossing the information with both formats and notch codes. However, this information does not thoroughly and definitively identify the periods of use of specific supports for all the manufacturers.

Although the edge print "Nitrate" or "Safety" is a direct reference to the type of film support, a preserving duplication strategy may result in the duplication of those references onto the new film and lead to an inaccurate identification.

Regarding the information provided by notch codes, different perspectives exist since these are related to the kind of photographic emulsion or type of support. Apart from these considerations, notch codes do not provide reliable information since a complete survey of these codes does not exist. Moreover, it is still lacking accurate identification of the supports that that support reliable decisions.

Apart from these intrinsic marks created by the manufacturers, simple identification methods are applied by conservators and archivists on a routine basis since they are inexpensive and don't require technical analytic skills or equipment.

Chemical spot tests, diphenylamine, density and burning tests, are commonly used for identification of film-based negatives and motion picture film. These methods were first reported to have been applied in the plastics industry to identify plastics in their pure state without additives. However, since film negatives and motion picture films are composite materials with plasticized polymers in the support and with subbing layers, the results obtained by these methods may give false results. The diphenylamine chemical spot test is used to identify CN film supports. Although this spot test is reliable, some interference should be considered. Additionally, it has also been reported that contaminants can lead to false results; e.g. the presence of chromates in CN subbing layers gives a faint blue colour, which may affect data interpretation.

The identification of CN, CA and PET film supports may be carried out through a density test. However, the chemical decay of CA supports, and the presence of additives may alter the density of the polymers and yield inconclusive or false results. The flame test's

accuracy is also affected by the presence of additives; furthermore, there is no agreement on the description of specific colours and odours for each type of film support for interpreting data generated by this test. The diphenylamine test, the density and the burning tests are destructive, time-consuming and may give inconclusive or erroneous results. Moreover, the solvents and solutions used for identification and gases released from the burning test are toxic, demanding added safety conditions. As for the assessment of film collections and a preservation strategy for film-based negatives and motion picture film collections, it is crucial to perform an accurate assessment since the chemical decay of films may contaminate entire collections. Still, film identification and condition evaluation are complex, mainly when materials show no signs of degradation. Visual degradation symptoms attributed to CN and CA chemical and physical decay examples have been compiled and categorized in degradation charts and are used by conservators and archivists. These degradation charts provide valuable and accessible tools for evaluating degradation rates.

Beyond the methods here presented, assessment of films condition often relies on the experience of the person carrying out the observation. Evaluations will vary based on each individual's judgement. The assessment of film decay based on offgasing is also subjective since each person can react differently to the intensity of released odour. Furthermore, the spread of acidic gases (nitric or acetic) in a storage area will contaminate all surrounding material and curtail an accurate evaluation of the odours emitted by each negative (Horvath 1987). It is important to emphasize that, although nitric and acetic acid odours are a tool for identification and condition assessment of CA and CN films, they represent a health hazard (Patnaik 2007, 108,119). Illness symptoms caused by prolonged exposure to nitric acid and acetic acid during cataloguing of a photographic collection have been reported (Hollinshead et al. 1987).

With the aim of assessing the chemical decay of film-based negatives, the search for methods to perform semi-quantitative or quantitative measurements based on the evaluation of the release of acidic vapours has been done by using indicators. The decay of the plasticizers has been shown to interfere with these methods.

The specificity of acid-base indicators is crucial considering that several degradation products result from the decomposition of materials. For instance, the degradation products arising from the decomposition of plasticizers may interfere with the results, e.g. the decay of triphenyl phosphate that results in diphenyl phosphoric acid which is a strong acid (Matsumura *et al*. 2002). Since acetic acid is a weaker acid, the rise of diphenyl phosphoric acid will not give a straightforward correlation with CA films since the indicators will react to the total concentration of gases rather than a specific one (Matsumura et al. 2002). The results obtained with indicators also rely on the testing time, and calculation of the average time-weighted measurements allows obtaining the average of acidity released (Grzywacz 2006). It is necessary to establish an average time exposure once the acidic gases may chemically react and bleach the indicator providing erroneous results (Matsumura et al. 2002). The sensitivity to light (especially UV light),

temperature and storage time are also issues to be considered when selecting the type of indicator. Light and temperature may induce changes on the chemical reagents. In some cases, the active surface may be sensitive to light and undergo a colour change or fading (Hackney 2016).
Acidity, as a marker for CN and CA decay, has also been evaluated with potentiometric methods. The main drawbacks of the tests that have been used are their destructive nature and high cost.

Concerning the physical film degradation, quantifying the shrinkage allows assessing the decay in a non-destructive way.

In sum, this chapter presented the great variety of methods commonly used in photographic archives for film support identification but most importantly alerts to the flaws and misinterpretation that may result from their application. The dimension of the film collections demands fast and non-invasive techniques that allow identifying and characterizing hundreds of films. It is agreed that the acidification of cellulose ester films is the first degradation sign. In the following chapters, possible alternatives to these methods will be discussed, serving as a solution to this urgent issue in the conservation of photography collections: a quick, reliable and accurate method for plastic support identification.

Chapter 4

Preservation of film-based collections in Portugal: results of a national survey

Chapter 4 – Preservation of film-based collections in Portugal: results of a national survey

The advent of plastic negatives had a significant impact worldwide. However, when investigating the historical background of plastic negatives in Portugal, there is a knowledge gap as to their appearance and use. Given the ephemeral nature of these materials, in the framework of this research it was questioned "What is the scope of plastic negatives' collections in Portugal? And what is being made to preserve film collections in Portugal?" To access this information an online questionnaire was conducted with 13 participants from Portuguese institutions (private and public).
In this chapter notes on the rise and use of plastic negatives in Portugal is presented to place the selected collections in context for this study. Then, the results reached with the questionnaire are given to support the importance of this work. The results show that there are huge quantities of plastic negatives with cellulose ester base mostly from European producers that are currently held in Portuguese collections. The questionnaire revealed the majority of the respondents are photograph conservators with extensive years of expertise. The results show that the participants are aware of the preservation guidelines disclosure worldwide since they have elected the common methods used for identifying and assessing plastic negatives. According to the respondents, instead of using field tests, the detection of acid release is evaluated mainly by odour. Therefore, the results indicate that Portuguese caretakers are continuously exposed to safety hazards during the periods in which the assessment task is performed. In this way, it might be concluded that the preservation condition of the negative's is assured while the health of the caretakers might be in danger.

4.1. Notes on the advent and use of black and white film-based negatives in Portugal

Shortly after the invention of photography, in 1839 the daguerreotype and the calotype photographic processes were announced in Portuguese newspapers, *O PANORAMA* and *REVISTA LITTERARIA*, respectively (Sena,1998). Despite the disclosure of these processes in the newspapers, the advent of photography was received with some disinterest by Portuguese society (Sena 1998, 21). The Portuguese political, economic and cultural context at the beginning of the 19th century may justify the lack of interest in photography (Sena 1998; Tavares 2010b). As António Sena[82] wrote:

> […] *the dissemination of new means of producing and reproducing images - photography - is at least as exalting as it is disturbing. In a country* (Portugal),

[82] Portuguese photograph researcher, founding member and director of the association *Ether/vale tudo menos tirar olhos*, dedicated to the study and dissemination of Portuguese photography.

> *startled by the rise and agony of liberalism* […] *which sought to industrialize without means, the appearance of two new technologies of image and text editing would represent an unusual challenge.*[…] *(Sena 1998, 13)*.

The two 'new technologies' referred to by Sena were photography and lithography[83]. At that time these technologies challenged and divided Portuguese society, while some accepted the new media and its innovative nature, others saw it as […] *an eccentric object in a country in obvious political, economic and artistic embarrassments* […] (Sena 1998, 44). Moreover, the costs and complexity of the initial photographic processes may have restrained its acceptance and use in Portugal. Nevertheless, photography gradually mustered up the attention and recognition of Portuguese society.

As reported in other countries, photography in the 19th century was commonly used to perform portraiture, landscape photography, and also documentary photography (Sena 1998; Sousa et al. 2008). The '*commercial impact and success'* of portraiture in Portugal was similar to the success attained all over Europe, where it was the high social classes that could 'afford' to take their photographic portraits (Sousa et al. 2008, 15; Tavares 2011). It also served other applications for instance portraiture progressively gained ground with government as a tool for criminal identification (Sena 1998, 50). Simultaneously, landscape photography (urban and rural views) and photographic surveys of heritage sites were two commercial routes taken to explore the aesthetics in photography, and immensely appreciated by the Portuguese public (Sena 1998; Tavares 2008, 13).

Over time, the wide acceptance and use of photography initially led to the establishment of photographic studios in the main cities, Lisbon and Oporto, and later spreading to the countryside (Sena 1998, 27, 37; Barradas 2015, 19). It is necessary to emphasize the important contribution that foreign photographers had on the acceptance of photography in Portugal. The Emílio Biel or Alfredo Fillon photographic studios are examples of the advent of commercial photography in Portugal, where they attained the awareness and respect of Portuguese society (Tavares 2010a, 75) and made headway for other photographic entrepreneurs. At the same time, Portuguese newspapers and magazines also helped to widely spread acceptance by disclosing inventions and innovations, as well as presenting translations and reports regarding technical issues, and advertising photographic materials and equipment.

Beside the breakthroughs accomplished in the field of commercial photography, Portuguese technical and scientific groups also accepted and used photography as a new *media* to register their work (Sena 1998, 21; Tavares 2010b). As Luís Miguel Bernardo[84] wrote:

[83] Printing technique for which materials varied overtime.

[84] Professor at the University of Oporto, director of the Museum of Science of the University of Oporto.

> *It was mainly in institutions of technical services or scientific research that the photographic techniques and other subsidiary techniques* (photomechanical processes)*, more easily settled and developed between us. (Bernardo 2014, 9)*

Considered […] *as a scientific proof* […] (Serén 2011, 184), photography was used to document the works in several scientific fields such as medicine, cartography, meteorology and geomagnetism, etc. as well as to document technical works in Portugal and overseas colonies (Sena 1998; Costa and Jardim 2014; Vicente 2014).

Throughout the 19thcentury and the 20th century, photography was also a chosen *media* to record Portugal's political, social, anthropological and ethnographic aspects, and for documenting the imperialist presence of Portugal in Africa and India (Sena 1998; Vicente 2014). In the political context, and with an enormous repercussion on Portuguese society, since 1932 until the 1970s photography became one of the most important tools for the propaganda strategy of the New State (Estado Novo) dictatorial regime, led by Oliveira Salazar (1889–1970) and António Ferro (1895–1956) (Sena 1998, 247; Tavares 2008, 2).
After several decades in which photography was only used by those who could financially support it or had the scientific knowledge to do it, the '*simplification*' of photography was accomplished due to technical developments and mostly due to the invention of film-based negatives began to be widely enjoyed in Portugal (Sena 1998, 147). The 'simplification' of photography was widely enjoyed in Portugal, leading to an increase in number of amateur photographers and photography clubs e.g. Foto-Club 6x6 (Sena 1998; Tavares 2008). Hence, the broadening of the market and the vast applications of photography became widespread in Portugal (Sousa et al. 2008).
An in-depth and broad description of different photographic and photomechanical processes existing in Portugal in the 19th century and 20th century is given in Sena's book, *História da Imagem Fotográfica em Portugal - 1839–1997* (1998) and in Fernanda Madalena Costa[85] and Maria Estela Jardim[86] book (2014), *100 Anos de Fotografia Científica em Portugal (1839 - 1939)*. It clarifies how these processes were used by Portuguese photographers (amateurs and professional), researchers, technicians and artists.
However, by reviewing the literature it was possible to conclude that, despite the increasing interest and diffusion of photography in Portugal, there were only two Portuguese companies producing photographic materials, PINHEIRO D'ARAGÃO & C.ª, in Oporto (Sena 1998, 147), and *A Portugueza*, in Lisbon (Araujo 2008, 1154). According to an advertisement shown in Fig. 4.1 the PINHEIRO D'ARAGÃO & C. ª produced only dry plate negatives designated as *CHAPAS PHOTOGRAPHICAS* (photographic plates) (Boletim Photographico 1900; Sena 1998, 147). Regarding *A Portugueza* products, no information was found.

[85] Member of the Research Centre CCMM - Centre for Molecular and Materials Sciences and collaborator of the Centre for Structural Chemistry, University of Lisbon.
[86] Membro integrado do Centro de Filosofia das Ciências da Universidade de Lisboa (grupo de investigação Ciência e Arte) e membro colaborador do Centro de Química Estrutural da Universidade de Lisboa.

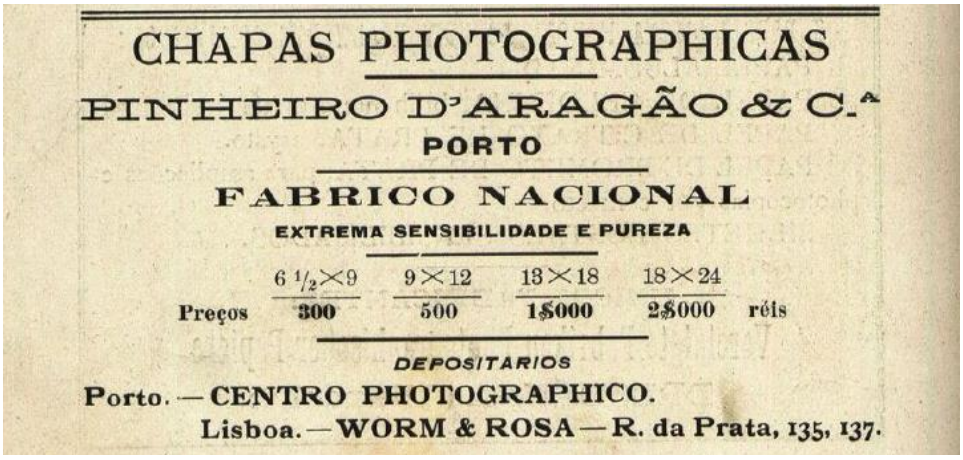


Figure 4.1 – Advertisement of glass plate negatives from the only Portuguese photographic materials manufacturer PINHEIRO D'ARAGÃO & C.ª (adapted from Boletim Photographico 1900).

Therefore, it is possible to consider that in Portugal, all photographic materials commercially available (e.g. film-based negatives, developing-out-prints) were imported. Fig. 4.2 shows an advertisement through which it is possible to see the variety of photographic materials and equipment commercially available in the Portuguese market in 1900. Most of the brands/producers disclosed in the advertisement are from other European countries.

Figure 4.2 - Advertisement of photographic materials and equipment produced by several manufacturers, published in the Portuguese photographic journal, BOLLETIM PHOTOGRAPHICO Nº8, from August 1900 (Boletim Photographico 1900).

By comparing the information about other photographic materials it was found to be a knowledge gap about the advent of plastic negatives in the Portuguese market (Tavares 2010b; Tavares 2008; Sousa et al. 2008; S. L. Marques 2015; Vicente 2014; Pavão 1997). In

part the gap may be related with the vague use of terms such as 'cliché' in which the type of image is indicated (negative) and not specifically a type of photographic process. With the aim of filling that gap and identifying the beginning of plastic negatives in Portugal a search was made with the terms 'Film' or 'Pelliculas'[87]. Based on the references of the aforementioned terms, and by crossing those with references and descriptions focused on the use of film-based negatives it was possible to identify that Aurélio da Paz dos Reis (1862 - 1931) documentary film shoot in 1896 is the first reference to the use of film, or more precisely motion picture film, in Portugal (Sena 1998, 184). Thus, it is believed that, a few years after nitrate-based negatives were invented (in 1889), motion picture film was already known by the Portuguese public. However, it was not confirmed if at that time film was already being commercialized in Portugal. This issue deserves further investigation. Besides the entertainment industry, the application of X-ray film in medical research performed by António Egas Moniz[88] (1874 – 1955) and the invention of angiography in 1927 is also emphasized (Sena 1998, 243, 244; Buzzi 2004; Pereira 2014). In the full description of the process, Moniz specifies to have used 'film' to capture images from the blood vessels of the brain (Egas Moniz as cited in Sena 1998, 244). Moniz outstanding achievement shows the importance of 'film' in medical research accomplished in Portugal. Another particular reference to the use of 'film' is attributed to António José Martins (1882-1942), who, in the 1930s, during an expedition to Newfoundland, used infrared film to photograph polar landscapes (Sena 1998, 245; Marques 2015, 219). In the same decade, Elmano Cunha e Costa also describes the use of film-based negatives in an expedition carried out in Angola[89] (Elmano Cunha e Costa 1943, 101). Some years later, in the 1950s, Victor Palla (1922–2006) and Manuel Ramos Costa Martins (1922-1996) described the photographic equipment and film-based negatives used to document numerous scenes of Lisbon that resulted in a seven-volume photobook, 'Lisboa, cidade triste e alegre' (Marques 2005, 114).

Nowadays, as the study and treatment of photography collections progresses, it is possible to know the extent of negative film collections, e.g. the Catalogue of Artur Pastor exhibition in which complete description of the type of films and formats used are presented. These references definitely give a short timeline on the use of film-based negatives (motion picture and still films) in Portugal, indicating that film started to be used in Portugal in 1896, few years after its invention in 1889. Advertisements and technical texts in which protocols and recommendations present in photography

[87] During this study it was found the need to clarify the terms or designations given to indicate the different types of photographic processes. In sum three generic references were used being the term 'CHAPAS' used to indicate glass plate negatives; 'PAPEIS' was the term for the broad type of photographic prints, and 'PELLICULAS' the designation given for film-based negatives. Despite the common use of these terms on the literature a clarification on these was consolidated by readings of Portuguese photography magazine (e.g. Boletim Photographico) and advertisements of photographic materials. The term 'Cliché' was also found to indicate a negative but not specifying which type of support.

[89] Detailed information about Cunha e Costa collection is presented in Chapter 5.

magazines may also contribute to establishing a timeline on the use of plastic negatives as well as a broader knowledge about the brands marketed in Portugal at the beginning of the 20th century (Fig. 4.3).

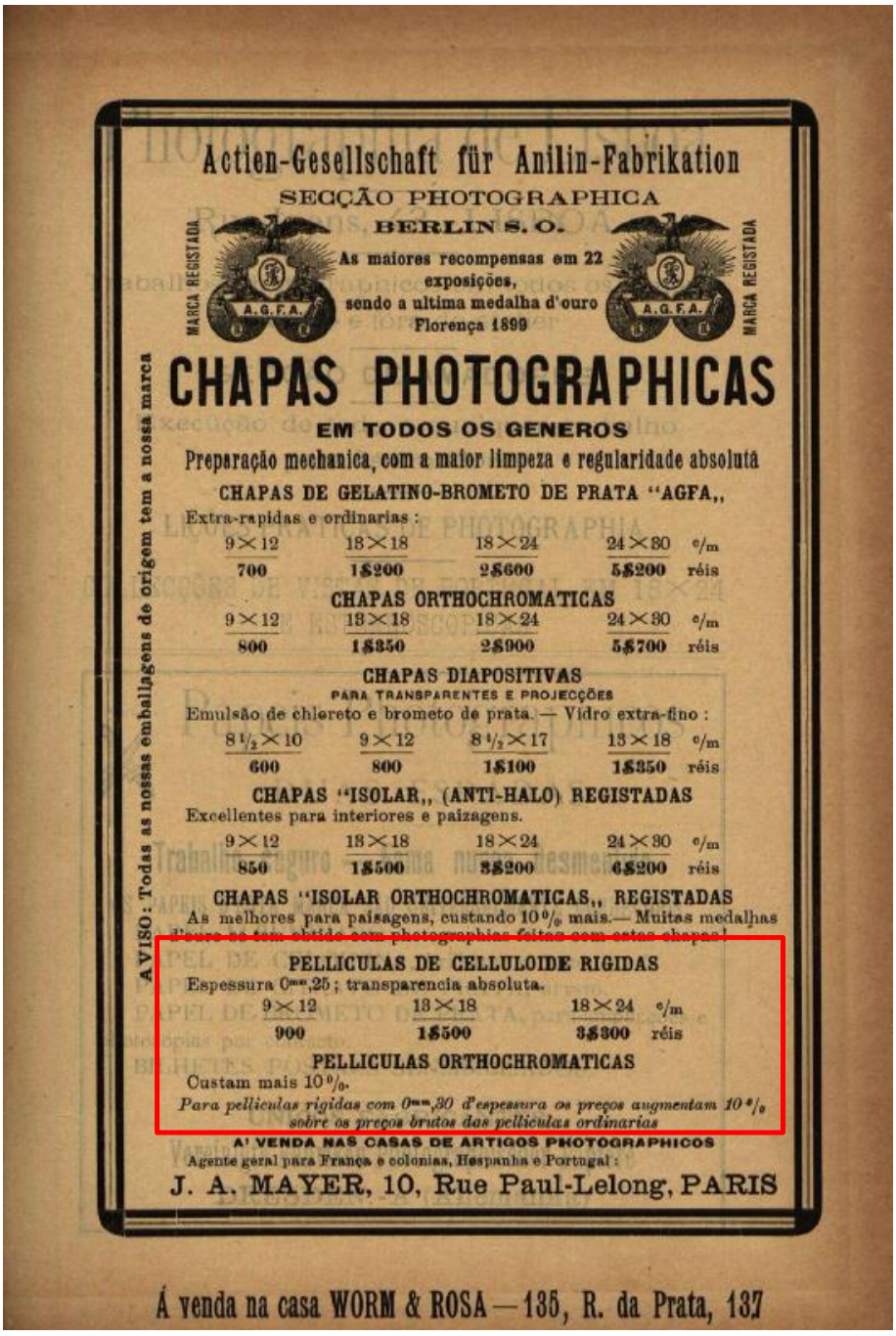


Figure 4.3– Advertisement to Actien-Gesellschaft für Anilin- Fabrikation (A.G.F.A.) dry plate negatives (CHAPAS PHOTOGRAPHICAS), celluloid film and orthochromatic film (red box), published on the Portuguese photographic journal, BOLLETIM PHOTOGRAPHICO, from 1900 (Boletim Photographico 1900).

For instance, as shown in Figures 4.2, a wide variety of producers, e.g. Eastman, Ilford, Wellington and Actien-Gesellschaft für Anilin- Fabrikation (A.G.F.A.), were sold in Portugal. In Fig. 4.3 an advertisement of AGFA show the variety of products sold in the

1900, e.g. *Celluloid Film* (Pelliculas de Celluloide Rigidas) and *Orthochromatic Film* (Pelliculas Orthochromaticas) (Boletim Photographico 1900). Photographic magazines (e.g. Bolletim Photographico and Echo Photographico[90]) and reports from photographers elucidate about the film-based negatives used since the late 19th century. The expedition report written by Elmano Cunha e Costa is one example of the relevancy of historical documentation that provide in depth information the photographer work. Additionally, as found for the San Payo collection, exhibition catalogues may also contribute for a (total or partial) disclosure of photographer's working materials. Nevertheless, and according to the purpose of the exhibition, the information provided on the exhibition catalogues do not scope the overall working periods of the photographers. The information found in these publications became crucial for an in-depth knowledge of the materials and photographers' techniques, which support the results obtained throughout this study. However, and despite the efforts performed, there are still lacking comprehensive studies that besides focusing the aesthetic and artistic work of a photographer, complement it with providing information concerning the materials a photographic method of the photographers.

In sum, concerning the history of photography in Portugal, it was found that the identification and conservation condition of early photographic processes present in Portuguese collections have been investigated (Sena 1998; Sousa et al. 2008; Costa and Jardim 2014). However, this study has not been carried out in a systematic way. Despite the investments made on historical and technical research carried out mostly since the 1990s (Tavares 2008, 3), few references were found concerning plastic negatives or plastic negatives collections. This fact does not suggest a lack of investment in conservation and preservation of plastic negatives but rather a lack of systematic disclosure of collected information during the surveys and conservation interventions carried out in Portuguese institutions. Unfortunately, absence of information about these materials restricts the build-up of a wider knowledge on film typologies within Portuguese collections.

Therefore, with the aim of understanding the Portuguese panorama concerning the topic discussed within this section, a questionnaire thought which the issues concerning the present identification and assessment methods currently carried out by Portuguese caretakers was performd. In this questionnaire the profile of those caretakers was performed. Moreover, a survey of film typologies and brands, present condition of film-based negatives collections and preservation strategies carried out within Portuguese public and private institutions was carried out. The results obtained are presented in the following section.

4.2. Black and white film-based negatives with cellulose ester support: the Portuguese panorama

4.2.1 Introduction

As presented in the previous chapters, the preservation of plastic negatives collections is an arduous and demanding task due to the ephemeral nature of these negatives and owing to the enormous quantities of such specimens in collections. Conservators and overall caretakers preserve these collections by carrying out different methods to identify and assess the plastic negatives base. The execution of simple identification methods, macro assessment and monitoring tasks rely upon the existence of staff. An in-depth knowledge of this type of materials is demanded due to the variety of cellulose esters used as the film base and owing to the heterogeneous decay of these materials. Furthermore, the drawbacks reported for macro assessment and field tests may lead to misinterpretations that in a worst-case scenario come to a catastrophic loss of film collections. Therefore, additional research is demanded to contribute to improving the knowledge of films-based negatives and consequently improve preservation guidelines in order to accurately take decisions. As previously said, a substantial number of plastic negatives present in collections is challenging. Therefore, the discovery of new analytical methods, non-destructive, to identify and evaluate a large number of samples remains highly desired in the field of preserving film negatives.

These issues have been addressed in several international publications; however, less is known about the Portuguese film collections. Additionally, the actions taken by Portuguese conservators and overall caretakers to preserve those collections are not known. Therefore, in the framework of this study, it was questioned what type of plastic negatives and respective quantities are there in Portuguese film collections. Moreover, it was also questioned how do Portuguese photograph conservators, archivists, librarians and overall caretakers perform the identification, assessment and monitorization of film collections. Based on these questions, a survey was implemented by sending a questionnaire to a total of 15 Portuguese archives, libraries, museums and private institutions, where 13 have anonymously replied.

4.2.2 Materials and methods

An electronic survey, designed with a formulary by Google Drive,® was carried out with the aim to obtain data concerning the presence and condition of plastic negatives in Portuguese institutions. This survey was filled online. It was anonymous, and it allowed for collecting data automatically and later compile it in a database.

It was decided to present mainly close-ended questions, asking the respondents to select among a set of answers (Kazi and Khalid 2012). The option 'Others' was also included to obtain the expressiveness of the participants. Furthermore, precoded questions with

ranges of numbers were presented. These questions require no writing and are easy to answer. Additionally, data collected with close-ended and precoded questions are easier to quantify and analyse (Oppenheim 1992). Besides the questions restrained to Yes/No and precoded questions, the respondents could select more than one option from the set of answers. Therefore, in these cases, the total number of responses will add up to more than 100%. Additionally, in two questions the respondents were invited to indicate the literature upon which they support the identification of notch codes and the archival conditions currently implemented in the institutions.
In Fig. 4.4 the layout of the questionnaire and the straightforward process of selecting the responses is displayed.

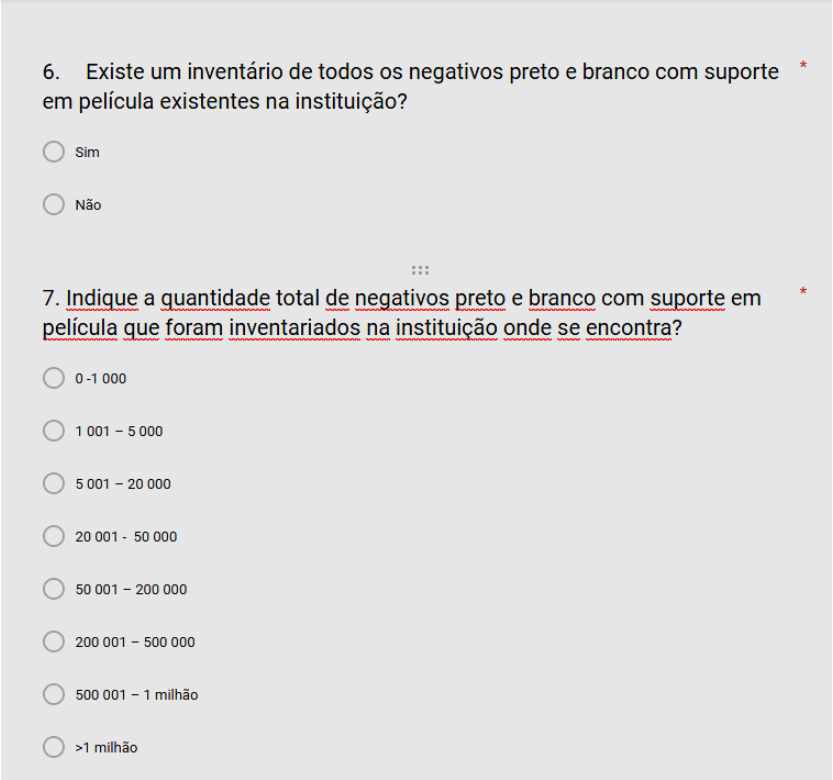


Figure 4.4 – Part of the questionnaire layout as it appeared online. Mandatory questions are indicated with an asterisk (*).

With a total of 31 questions, the first four questions are focused on the type of institution and the respondents' profile. The remaining questions focus on the identification of plastic films (typology and quantities) in the archives, simple and macro identification methods currently used to identify and assess the film decay, identification of producers/brands, and conservation and preservation strategies currently implemented in the institutions, where respondents work. Regarding the questions aimed at the respondents' profile, two questions are focused on the respondents and one on the identification of the type of institution. The following questions presented in section 4.2.3.2. enfold the issues related with plastic negatives inventory in order to assess the quantity, types and brands of films present in Portuguese collections. The questions

covering the 'Currently used methods for identification and assessment of plastic negatives condition' are addressed in section 4.2.3.3. The questions were designed according to the preservation and identification guidelines presented in Chapter 3. These guidelines support the design of questions that deal with the 'Present condition grade and preservation strategy' presented in section 4.2.3.4.

The survey, considering the target population, was written in Portuguese and later translated into English in this work. The questions were addressed according to the technical terminology used in Portugal, and then translated according to the terms generically used in the literature (Pavão 1997; Eaton, Bard, and William 1985; Fischer and Robb 1993; Lavédrine 2003; Valverde 2005).

This questionnaire was sent by email to 15 Portuguese institutions mostly in the Lisbon area in 2017. This questionnaire was directed to every caretaker responsible for the conservation and preservation of film collections. The answers obtained were not segmented according to the profile of the answers since the questions presented in the questionnaire are transversal to all film caretakers.

4.2.3 Results and discussion

4.2.3.1. Respondents profile

Table 4.1 summarises the profile of the survey's respondents.

Table 4.1- Profile of the survey's respondents

	Segment	% of respondents
Professional activity	Archivist	30
	Conservator (senior)	39
	Conservator (junior)	23
	Conservation scientist	0
	Collection manager	0
	Curator	0
	Historian	0
	Librarian	0
	Other	8
Type of institution	Archive	69
	Museum	8
	Library	15
	Private collection	8
	Other	0
Years of experience	0-4	0
	5 - 9	23
	10-19	62
	>20	15
Photograph Conservators	0	38
	1-3	62
	4-6	0
	>6	0

According to data collected, the majority of the respondents were senior Conservators, followed by Archivists and junior Conservators. The majority of the participants work in public Archives, Libraries and Museums and only one respondent answered working on a private collection. Out of the 13 participants, most of the participants had 10 to 19 years of experience. Surprisingly, the results indicate that there are no photographic materials conservators with less than five years of experience working in Portuguese institutions. This result allows suggesting that recently graduated and pos-graduated students are not working in the field of photograph conservation.
Moreover, it was also questioned how many photograph conservators work permanently in the institutions (public or private). The majority of the participants indicated that they had 1 to 3 photograph conservators working permanently in their collections. However, 38% replied not to have photograph conservators in their institutions. In this way, it is possible to suggest that there are other caretakers (e.g. archivists and librarians) that might be responsible for film-based negatives collections.

4.2.3.2. Plastic negatives inventory

Table 4.2 shows the percentage of responses to the questions on the inventory of plastic negatives.

Table 4.2- Percentage of responses to the questions that require a Yes/No response

Question	Yes (%)	No (%)
Does your institution hold black and white film-based negatives?	100	0
Is there an inventory covering the totality of black and white film-based negatives existing in the institution?	54	46

Participants were first asked to indicate if their institution holds black and white (b/w) film-based negatives in their collections. All participants confirmed to have plastic negatives in the collections. To understand if the participants were aware of the total quantities of plastic negatives in the collection, it was asked if there is an inventory of the whole collection. The participants were then asked to specify the range of negatives inventoried. The results obtained may be related with the overall inventory or with partial inventories that have already been done. Despite the close percentage of answers, 54% answered to have performed the total inventory of the collection while 46% is not aware of the typologies and preservation condition of the negatives within the collections (Table 4.2). Due to the ephemeral nature of CN and CA based negatives, this result is an alert for the needs of Portuguese institutions.
Fig. 4.5 shows the percentage of responses to the mandatory question 'What is the range of film-based negatives inventoried in your collection?'

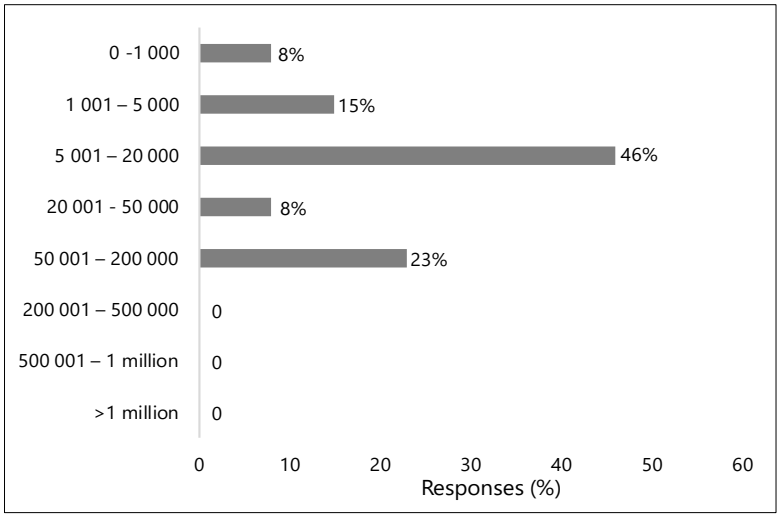


Figure 4.5 – Percentage of responses to the mandatory question 'What is the range of film-based negatives inventoried in your collection?'

According to data collected the majority of the respondents answered to have inventoried from five thousand to 20 thousand film-based negatives. This data allows to confirm the extensive use and presence of plastic negatives within the collections that replied to the questionnaire.

Additionally, these results suggest that not all institutions are able to do the overall inventory of the plastic negatives collection, possibly due to the huge amounts of specimens and/or lack of staff to perform the task. Moreover, the 'partial inventory' of the collections may also be related with the conservation and preservation interventions that are progressively carried out in the institutions since, by comparing the results presented in Fig.s 4.5 and 4.6 it is possible to find a gap between the range of quantities of plastic negatives inventoried and treated.

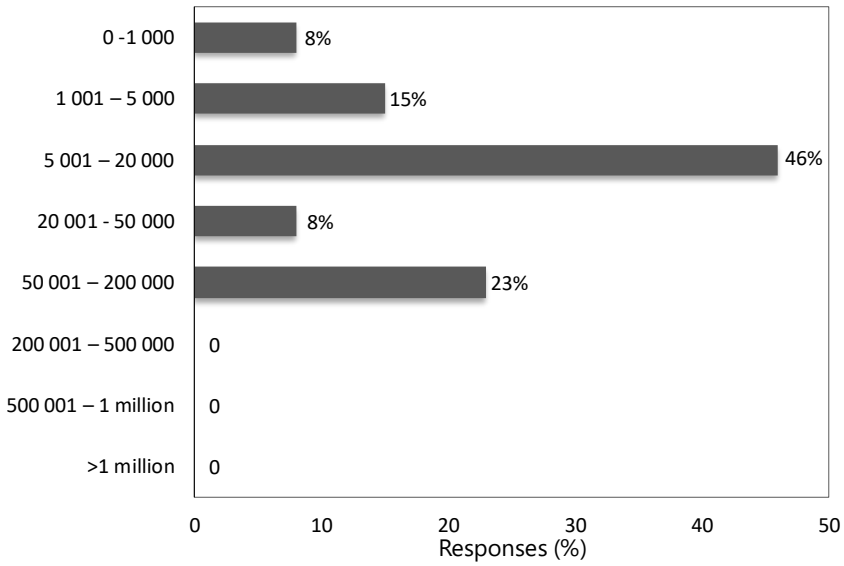


Figure 4.6– Percentage of responses to the mandatory question 'What is the quantity of b/w film-based negatives that have already undergone conservation and preservation interventions?'

Participants were requested to specify the quantities of CN and CA film-based negatives in their collections. Table 4.3 summarizes the range of CN and CA film-based negatives indicated by the participants.

Table 4.3 - Percentage of responses (%) to the questions 'What is the estimated amount of CN and CA film-based negatives present in the institution?'

Range	CN* (%)	CA* (%)
0 – 1 000	39	23
1 000 – 5 000	30	23
5 001 – 20 000	23	8
20 001 - 50 000	8	23
50 001 – 200 000	0	15
> 200 000	0	8

According to the participants' answers, there is a higher amount of CA film-based negatives in Portuguese institutions (Table 4.2).
Furthermore, from a list of options, the participants were asked to select the brands/producers inventoried in their collection (Fig. 4.7).

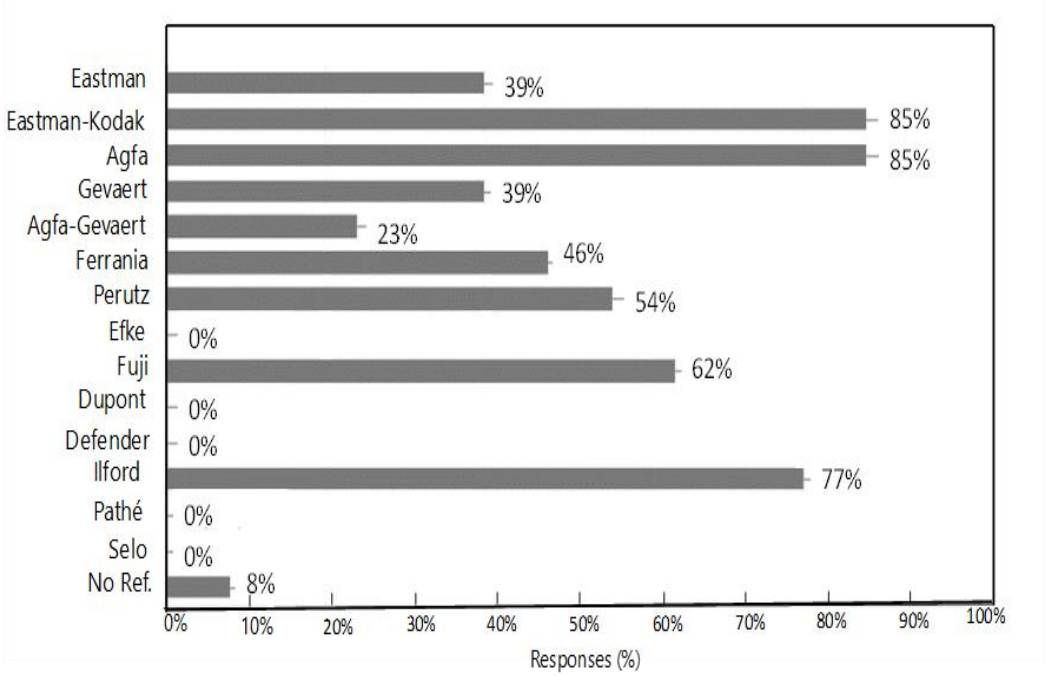


Figure 4.7- Percentage of responses to the mandatory question 'Which film brands/producers are there in your collection?'

The results reflect the film brands/producers represented in Portuguese film collections (Fig. 4.7). Except for one participant, who indicated the presence of films lacking brand identification, the other participants included the brands already identified during the inventory. From the total brands indicated, Eastman-Kodak and Agfa are the most

common brands in Portuguese collections followed by Ilford, Fuji, Perutz, Ferrania, Gevaert, Eastman and Agfa-Gevaert, respectively (Fig. 4.7). Additionally, none of the participants indicated the presence of Efke, Dupont, Defender, Pathé or Selo. Therefore, it is possible to conclude that besides Eastman, Eastman-Kodak and Fuji, the common film-based negatives present in Portuguese collections are from European producers. Furthermore, comparing the results obtained with the references given in Table 2.2, besides Kodak there are no references to the producers indicated by the respondents. Therefore, these results confirm the presence of several film brands, especially European brands, in Portuguese collections. Again, these findings allow to reaffirm the need to contribute and invest in further research to gather in-depth knowledge about the history of commercial film production in Europe.

4.2.3.3. Currently used methods for identification and assessment of plastic negatives condition

Following the guidelines proposed in the literature (please see Chapter 3, sections 3.2 to 3.7) the participants were asked about the methods used to identify and assess the condition of film-based negatives.
Firstly, the participants were requested to indicate if they support the identification of the film base on the dates given by the photographers.

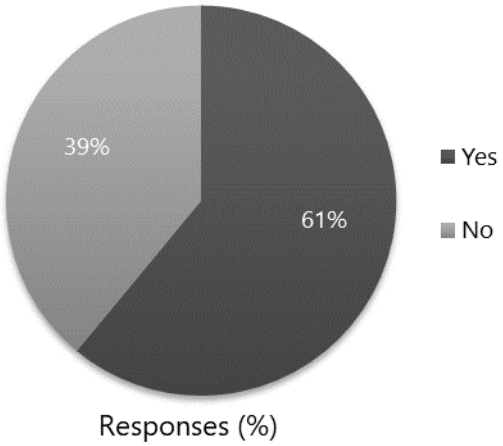


Figure 4.8 - Distribution (%) of responses to a question concerning the use of dates for supporting film base identification: 'Do you support the identification of cellulose ester photographic negatives on the dates given by photographers? *'

61 % of the respondents answered supporting the identification of the base of the film on the dates given by the photographer (Fig. 4.8). As explained above, the Portuguese market seemed to have enjoyed from the broad commercialization of film-based negatives. However, since these films were produced by foreign companies, a gap between dates of production and market sale may have exhisted. This issue must be considered nowadays since it may led to incorrect identification. Furthermore,

respondents were asked to select other criteria (degradation signs, field tests, etc.) on which they support the identification of the film base. Fig. 4.9 shows the results reached.

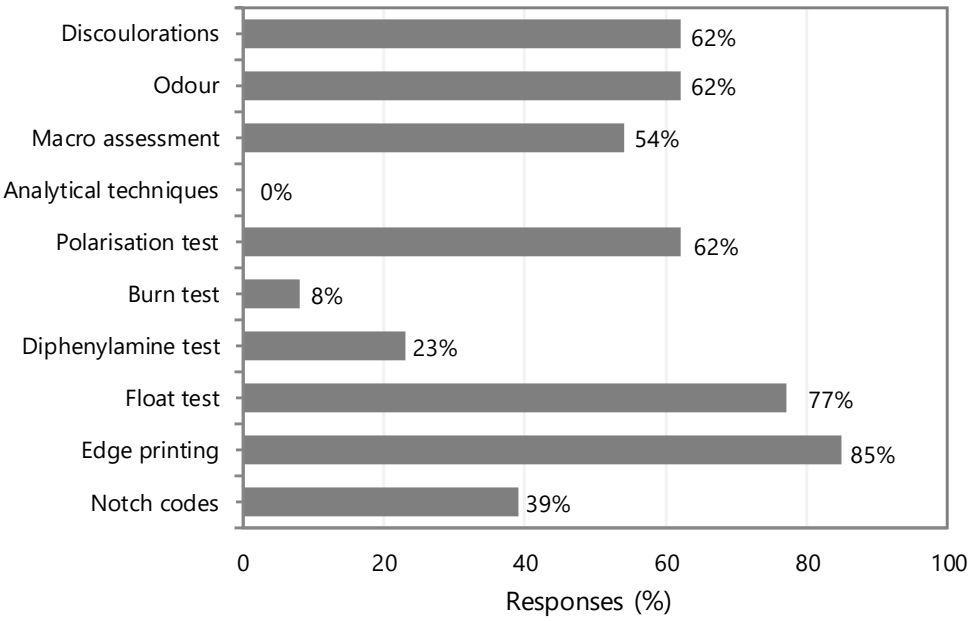


Figure 4.9 - Percentage of responses (%) to the question 'Which criteria do you use to identify cellulose ester plastic negatives? *'.

It was given the possibility of electing analytical techniques however it was not specified any since the intention was to broadly understand if Portuguese caretakers are currently using (or not) any analytical technique for film base identification (Fig. 4.9). None of the respondents indicated the use of analytical techniques for film identification.

According to the answers obtained, participants support the identification based on edge printing (85%) 'Nitrate' and 'Safety' designations, and density test (77%). A minor use of burn (8%) and diphenylamine (23%) tests was pointed out by the respondents. As previously said these tests may lead to incorrect identification. Additionally, respondents also indicated supporting the identification on degradation signs generically indicated as macro assessment (54%), highlighting also discolouration and odour (62%). This result points out for the subjectivity f the parameters used, but more importantly for the health risks to which caretakers are submitted due to the prolonged exposure to acidic gases released by degraded plastic negatives.

Only 39% of the respondents indicated the use of notch codes for identification of plastic negatives. The participants were requested to specify the notch codes reference on which they base the film support identification. This was not a mandatory question since only four replied. Three of the participants indicated the notch code list given in Luis Pavão's book (1997) (please see Appendix II), while one of the respondents replied saying he/she is not aware of any guideline or list for notch code identification.

Despite the respondent's indication of the use of macro assessment, discolouration and odour, when specifically asked if they believe that macro assessment allows an accurate identification of the film base all participants (100%) replied 'No'. Therefore, it is believed

that despite the inherent inaccuracy of some parameters, Portuguese caretakers have to support their decisions or film identification on first level identification criteria (that sometimes may be definitive since none performs analytical methods). With the aim to find out which general guideline(s) the participants support the macro assessment of film-based negatives, they were asked to answer the question: 'On which reference do you support the macro assessment of the conservation grade for plastic negatives?' (Fig. 4.10). This was not a mandatory question since only seven replied.

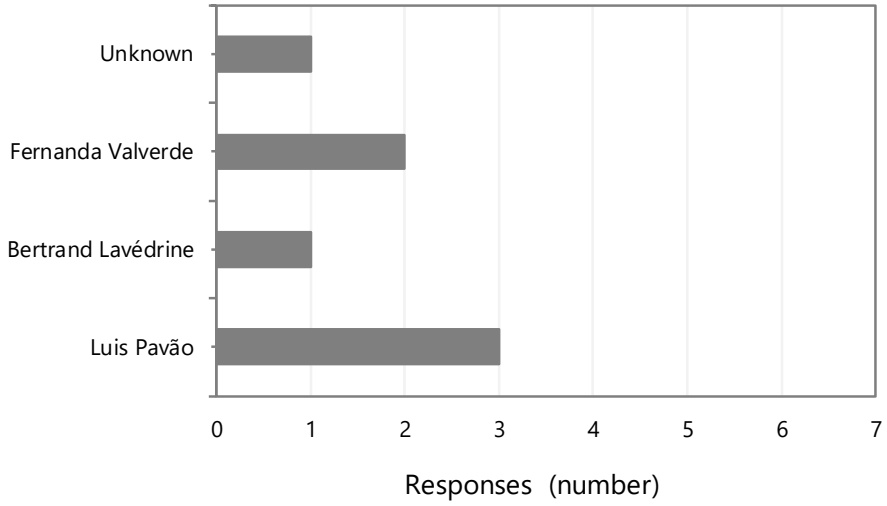


Figure 4.10 – Number of responses to the solicitation 'On which reference do you support the macro assessment of the conservation grade for plastic negatives?'.

Luis Pavão, Fernanda Valverde and Bertrand Lavédrine were the references indicated by the respondents (Fig. 4.10). Moreover, one respondent indicated the lack of knowledge of references to perform the macro assessment film-based negatives. The consistent lack of knowledge about identification and macro assessment guidelines shown by one participant indicates that the respondent may not have the educational knowledge and skills to perform those tasks and therefore putting at risk the collection under which he/she is responsible for. These results also suggest that institutions do not always hire photograph conservators to treat the collections that they oversee.

Regarding the methods used for evaluating film negatives degradation, specifically to detect and evaluate the acidification of the cellulose esters film base, respondents were asked to indicate the methods used in their institutions. Fig. 4.11 shows the number of responses to the question 'What methods do you use to detect and evaluate the acidification of CN film-based negatives?'

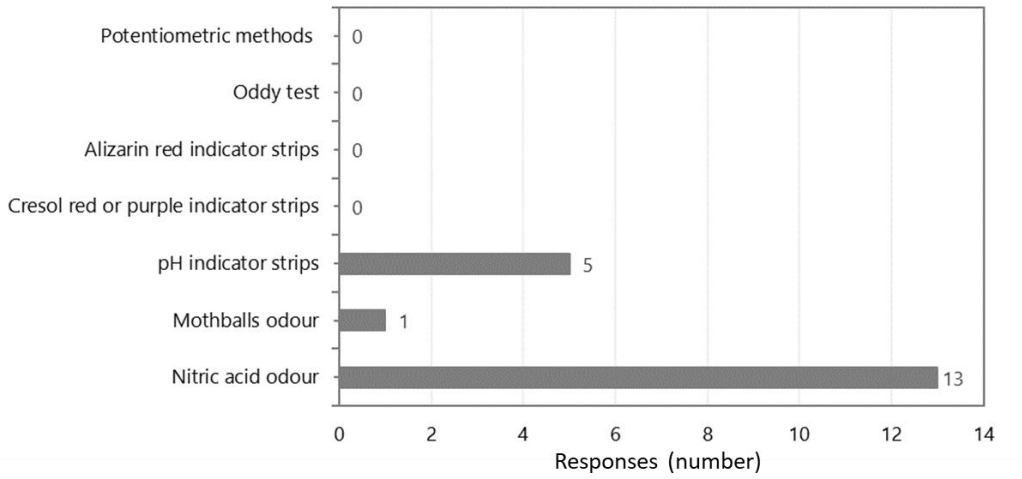


Figure 4.11 - Number of responses to the question 'What methods do you use to detect and evaluate the acidification of CN film-based negatives?'

From the seven options given only three were selected (Fig. 4.11). According to the results obtained, the participants support the detection and evaluation of CN films acidification mostly on the odour, putting themselves at risk. Additionally, for a semi-quantitative of CN film decay, participants indicate the use of pH indicator strips. Only one respondent indicates the detection and evaluation of CN film negatives decay based on mothballs odour. Based on the results obtained, neither potentiometric methods, Oddy test and alternative colourimetric methods (alizarin red, cresol red and cresol purple indicator strips) are used to assess the chemical decay of film collections in Portuguese institutions and private collections. Furthermore, the results indicate that when performing the identification and assessment of CN film-based negatives participants are continuously exposed to health hazards since the assessment is mostly based on the odour.

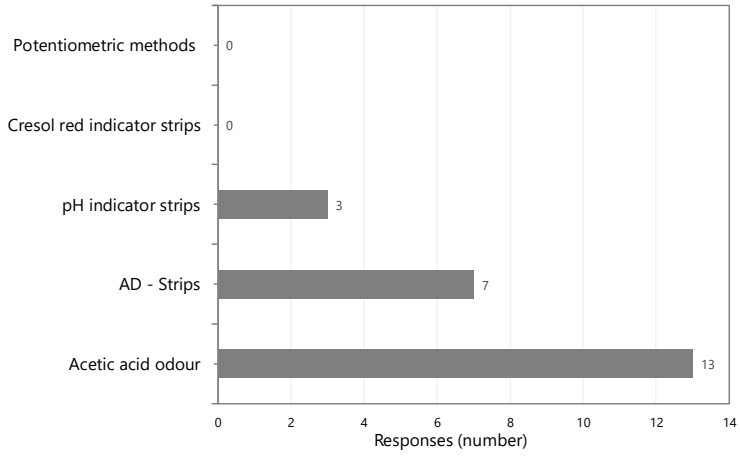


Figure 4.12 – Number of responses to the questions 'What methods you use to detect and evaluate the acidification of CA film-based negatives?'

Regarding CA film-based negatives decay, as presented in Fig. 4.12 all respondents indicated that they perform the assessment based on acetic acid odour, followed by the

use of AD-Strips and pH indicator strips. Again, the participants are continuously exposed to health hazards when assessing the collections.

4.2.3.4. Present condition grade and preservation strategy

Considering the volume of film-based negatives present in the participants collections, it was asked to specify the common degradation signs identified in those specimens. A mandatory question with a list of options was given, from which the participants could select more than one option.

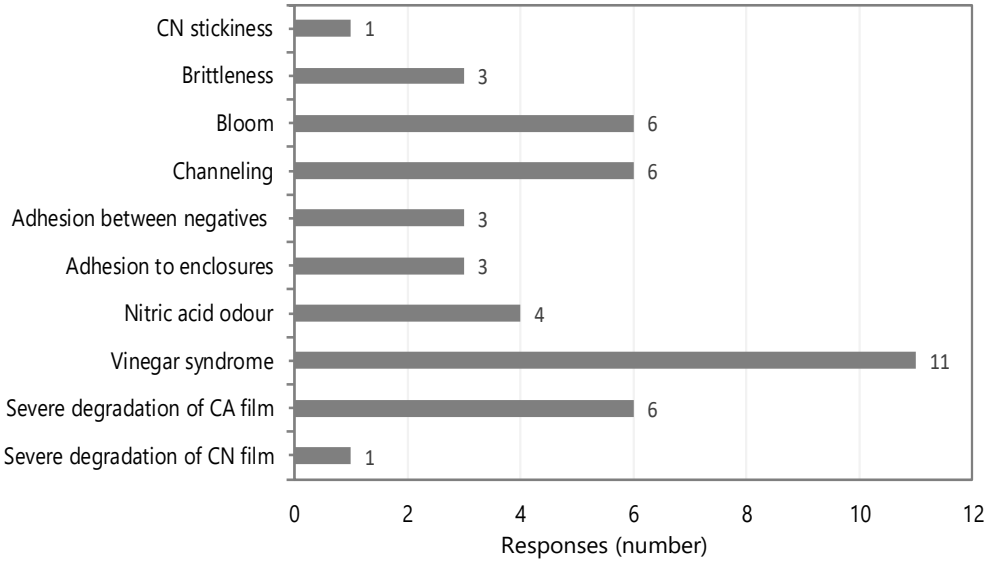


Figure 4.13 - Number of responses to the questions 'What are common degradation signs on your film collection?'

Fig. 4.13 lists the options given as well as the number of responses. According to the results obtained it is possible to suggest that severe decay of CA film-based negatives is more common than in CN films. Again, the odour is indicated as one of the most distinguishable signs of degradation, followed by visual signs as 'Bloom' and 'Channeling', both related with CA film-based negatives decay (Fig. 4.13).

Since the degradation of cellulose esters film-based negatives is autocatalytic and therefore a hazard for the whole collection due to the risk of cross-infection, participants were also asked which preventive actions were carried out in their institutions. Table 4.4 presents the frequencies of responses (%) given to the existence of storage rooms and preservation strategies for film-based negatives in Portuguese institutions.

Table 4.4 Percentage of responses to the questions focusing environmental conditions and preservation policies, that require a Yes/No response

Question	Yes (%)	No (%)
Do you have a quarantine room with ventilation and environmental control in your institution?	61.5	38.5
Do you have a definitive room with ventilation and environmental control in your institution?	54.5	45.5
Do you have a cold storage facility in your institution?	38.5	61.5
Is there a policy of cold storage for CN film-based negatives in your institution?	61.5	38.5
Is there a policy of cold storage for CA film-based negatives in your institution?	38.5	61.5

According to the results, 61.5% of the participants answered to have a 'quarantine room' with ventilation and environmental control in which untreated collections are kept until the beginning of conservation interventions. Regarding the 'definite storage room' in which treated collections are stored, 54.5% of the participants answered to have such room with suitable conditions to preserve cellulose ester film-based negatives. Comparatively, a lower percentage of participants (38.5%) answered to have a cold storage facility (Table 4.4). These results show that Portuguese institutions invest on environmental control to preserve the collections.

Table 4.5 Percentage of responses to the questions 'What is the criteria for storing CN and CA in cold storage facilities?'

Options	CN (%)	CA (%)
All	82	18
Only negatives with signs of degradation	9	64
Only severely degraded negatives	9	18

Additionally, regarding cold storage, the results reflect opposite behaviours towards CN and CA film-based negatives (Table 4.4). Moreover, the participants were requested to specify in which criteria do they prioritize the selection of the storage of film-based negatives in cold storage facilities (Table 4.5). According to data collected (see Tables 4.4 and 4.5), most of the participants (82%) show greater concern about CN film-based negatives preservation, indicating a clear tendency for storing all CN films in cold storage facilities (Table 4.5). It is believed that this tendency is based on the high flammability of CN films, which makes cold storage to be considered a method to control fire hazards. A different behaviour is seen towards CA film-based negatives since the majority of the

participants indicated to store mostly CA film-based that show signs of degradation in cold storage facilities (Table 4.5). However, 18% of the participants also answered to store all CA film-based negatives under low temperature conditions while another 18% of the participants answered storing only severely degraded CA films under the referred environmental conditions.

Participants were asked to indicate the environmental conditions adopted in their institutions. This was not a mandatory question thus only five participants answered it. According to the replies, three participants indicated having storage room with low temperatures (4 to 5ºC, and 9.5 ºC) and 35 to 40% ±5% RH.

The participants were also asked to indicate the annual cost associated with management and maintenance of storage rooms. All respondents answered not being aware of the costs (100% responses No).

Since some negatives and collections are heavily used, duplication or digitization are plausible options to avoid handling the negatives by allowing the access to the digital image. Therefore, the participants were asked if they consider digitization a preservation measure and if there is a digitization policy for film-based negative collections in their institution. Furthermore, the participants were asked to indicate the type of profile selected for digitization, if they use greyscale or RGB profiles. The percentage of responses is presented in Table 4.6.

Table 4.6- Percentage of responses to the questions focusing digitization policy for film-based negative collections (Yes/No response)

Question	Yes (%)	No (%)
Do you consider digitization a preservation measure for film-based negatives collections?	93	7
Digitization		
With grey-scale profile	23	
With RGB profile	77	

93% of the participants answered to see digitization as a measure to preserve plastic negatives collection, and 77 % answered to use RGB profiles. In opposition, only 7 % of the participants replied not to consider digitization a preservation procedure and 23% do digitize the collection in greyscale profile. These results indicate that the instructions that replied to this questionnaire are investing on digitization of the collections in order to restrict their use and at the same time for disclosure the collection. Additionally, by using RGB profile, the majority of the participants are creating files that in the future may allow to assess the discoloration of the degraded negatives. In this way, digitization may also be an assessment tool for the future monitorization of the negative's degradation.

4.3 Concluding remarks

In this study, it was questioned if the historical context of the production and use of films-based negatives in Portugal had been made. It was found that early photographic processes reached Portuguese historians and researchers' interest in opposition to film-based negatives that deserved only a few references in the literature. The ready-to-use nature of film-based negatives supported their broad acceptance, yet it may have also banalized these materials, leading those to be neglected by historians and researchers. Furthermore, by reviewing the literature it was possible to conclude that beside the commercial production performed by PINHEIRO D'ARAGÃO & C.ª and *A Portugueza*, there was no photography industry in Portugal. Nevertheless, apparently this had no implication in the generalization of the use of photographic materials.

The conclusions taken after reviewing the literature led to the necessity of carrying out an anonymous questionnaire[91] to screen the quantities and types of film-based negatives held by Portuguese institutions. The results have shown a wide variety and a large amount of negatives within those institutions.

According to the answers, the majority of the participants work in archives or libraries, and are mostly senior conservators with careers with more than 9 years. The results also allowed concluding that there are no conservators with less than 5 years of practice working on the conservation and preservation of film collections. 62% of participants answered to have 1 to 3 photograph conservators in their institution. These results show that institutions are investing on having human resources, conservators, that may maintain an ongoing treatment and preservation collections.

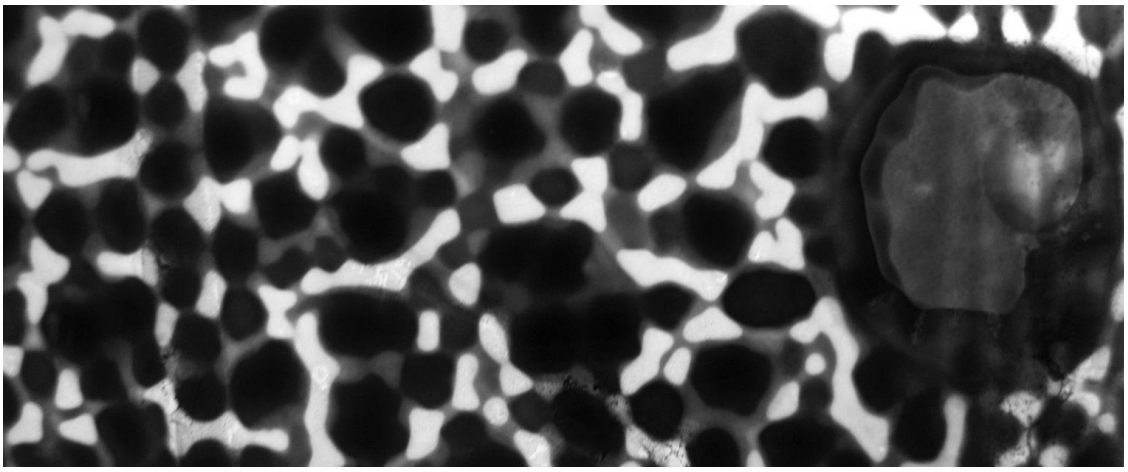
The results obtained with this questionnaire allowed to clarify the initial doubts formed during the review of the literature. According to data collected there are huge amounts of cellulose ester film-based negatives in Portuguese institutions, mostly produced by Eastman Kodak and several European producers.

Regarding the currently used methods for identification and assessment of plastic negatives conditions, the results allow proposing that Portuguese caretakers support the identification of plastic negatives based on the dates given by the photographer (that may lead to erroneous identification). Additionally, it was possible to conclude that the participants are aware of and use the guidelines proposed in the field of conservation of film-based negatives (see Chapter 3). Several reasons may be proposed but based on the results presented it is suggested that the criteria and selection of field tests rely on the low cost and simplicity of those tests. Furthermore, the main reference for film base identification and macro assessment is Luis Pavão's book. These results suggest that Portuguese caretakers selected their reference based on the native language or due to similarities found between the information provided in Pavão's book and the reality of

Portuguese archives. Furthermore, degradation signs are also a criterion to identify film-based negatives, which odour is one of the most resourced parameters to identify and assess negatives, however as previously said this may induce to errouneous identification due to misinterpretations of the signs of degradation.

According to the responses in the survey Portuguese caretakers and institutions are developing and implementing preservation strategies to safeguard film collections, similar to those indicated in international preservation guides. However, the risk of health hazard due to long-term exposure to acidic vapours must be considered in future research to prevent health problems in those working with these collections.

The results obtained with this questionnaire permit to screen Portuguese film collections and to contextualize the work carried out in this study and presented in the following chapter.



Chapter 5- Experimental

Chapter 5 - Experimental

5.1 Questionnaires

One questionnaire was designed and sent to national archives (11 institutions) and private institutions (4) that held film collections. General questions (total of 31) were posed focusing:

a) the type of institutions and the profile of the respondents (four questions);
b) issues related to plastic negatives inventory aiming to assess the quantity, types and brands of films present in Portuguese collections (seven questions),
c) simple and macro identification methods currently used to identify and assess the film decay (nine questions),
d) conservation and preservation strategies currently implemented in the institutions (11 questions).

With this questionnaire it was intended to access the current conservation and preservation of the film collections in Portugal.

5.2 Interviews

Two informal interviews were prepared and conducted with one Portuguese photograph conservator and a former worker of Agfa-Gevaert.

These interviews were carried out in-person and by writing (by email correspondence).

June 1st 2012 – Informal interview with Alexandra Encarnação, coordinator of the Arquivo de Documentação Fotográfica. Personal interview held at Arquivo de Documentação Fotográfica, in Lisbon and conducted by Élia Roldão.

September 5th - Informal interview with Willy Van Leemput, former worker and archive volunteer of the Agfa-Gevaert. Personal interview held at Lieven-Gevaert archive, in Lieven, Belgium, and conducted by Élia Roldão.

5.3 Workshops

One workshop was held at the laboratories of Arquivo Histórico Ultramarino on the methods currently used to measure pH on plastic negatives. The workshop was integrated in the disclosure action of the project "*Digitalização e Tratamento da Filmoteca Ultramarina Portuguesa – DigiT FUP Imagem Digital na dupla função de transferência de suporte e restauro documental*". *The w*orkshop was presented in 16th December 2014 (http://www.iict.pt/DigiTFUP/wsh.html).

5.4 Methodology

5.4.1. Criteria for the selection of collections and samples

The criteria for selection of collections and case studies are depict in Figure 5.1.

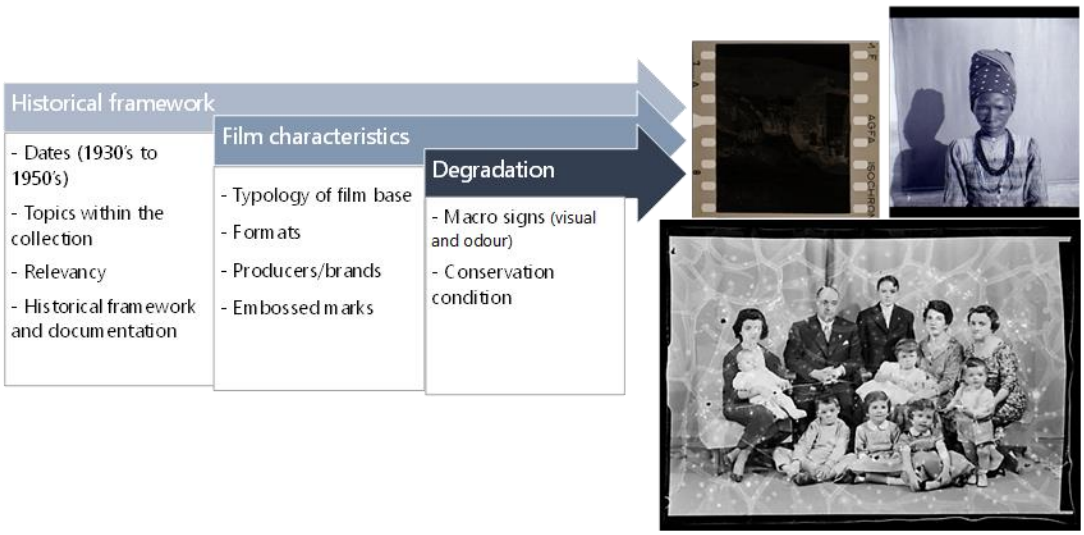


Figure 5.1 – Criteria on which relied the selection of the case studies (left). Examples of specimens selected from the collections with 35mm (a), 120 mm (b) and 13x18 (c) cm formats, and in 1,3 and 5 condition.

The selection of the institutions relied on their capability of providing information about the historical framework of production of the collections and also on the presence of film collections performed in the timeline established (1930's to 1950's). Five collections were included in this work aiming at getting a wide variety of film types, assorted formats and brands. The storage and environmental conditions (past and present) of the collections was also considered. Regarding dating, the information available relied mostly on the references disclosed by the photographers, thus depending on original organization. Original enclosures (sleeves or cardboard), indexes and historical documentation related with the collections were also usefull documentation. Regarding sample selection within each collection, firstly an observation of the collections was performed followed by a selection of the samples according to typology, brands, formats, embossed marks (edge printing and notch codes) and preservation condition. In this way, it was intended to gather a diverse type of films that could reflect the film negatives used in the past and assess their decay. Regarding the macro assessment of the collections, Table 5.1 was designed, summarizing in five-grade the degradation patterns commonly associated with negatives with CN and CA supports. By doing so, it was intended to establish an uniformization between the guideline charts found in the literature and indicated in the questionnaire carried out in the framework of this study (Lavédrine 2003; Valverde 1997; Fischer 1951; Pavão 1997).

Table 5.1 – Five-grade condition chart designed for evaluation and selection of samples/negatives for this study

Cellulose nitrate	Condition grade	Cellulose acetate
In excellent condition, without visual signs of degradation	**Very Good (1)**	In excellent condition, without visual signs of degradation
Minor signs of degradation visually detected (yellowing); light silver mirroring	**Good (2)**	Minor signs of degradation visually detected (yellowing, light blue and pink hues); light vinegar smell
Recognizable signs of degradation (amber); strong silver mirroring	**Fair (3)**	Visible signs of degradation, e.g. light warping of the peripherical areas of the negative, recognizable vinegar smell
Discolouration (strong brown hue); blistering; strong silver mirroring	**Deteriorated (4)**	Accentuated warping, blistering, bloom, weeping and leaching; strong vinegar smell
Discolouration (strong brown hue), negatives sticked between them or to enclosures; loss of emulsion and anti-curl layer; strong nitric acid smell	**Severely deteriorated (5)**	Channelling, brittleness and delamination

5.4.2. Macro assessment of the samples selected

Since a large set of negatives was selected, it was imperative to create e a system for recording the macro assessment results obtained. For that, a worksheet was developed in Microsoft Excel software® for recording the identification (indexation number), format and preservation condition of each negative selected for this study. Additionally, embossed marks (film identification, brands, and notch codes) were also recorded per negative. In this way it was possible to establish relationships and quantification of the data gathered.

5.5. Samples collected from the five collections scoped

The total number of case studies varied according to collection (it was not intended to establish a closed number of samples per collection) depending on the dates (whenever disclosed), film types, formats, and preservation condition. In Table 5.2, the amount of negatives selected per collection, the types of film supports, formats and preservation condition of those negatives is presented.

Table 5.2 - Amount of negatives selected, types of film supports, formats and preservation condition of the negatives, per collection.

Collection	Negatives selected (amount)	Film support	Formats	Preservation condition
Elmano Cunha e Costa (ECC)	99	CN	60mm	Very Good to Poor
Direcção Geral de Edifícios e Monumentos Nacionais (DGEMN)	49	CN	35mm, 60mm, 9x12 cm, 10x15 cm, 13x18 cm, 18x24 cm	Good to Severe
Mário Novais (MN)	1	CN	18x24 cm	Severe
San Payo (SP)	190	CN, CA	35mm, 60mm, 9x12 cm, 10x15 cm, 13x18 cm, 18x24 cm	Very Good to Severe
Silva Nogueira (SN)	22	CA	9x12 cm, 10x15 cm, 13x18 cm,	Very Good to Severe

5.6. Materials

5.6.1 Other samples

CDA and CTA model films were produced, and CN filtration membranes were used as references. Additionally, for the artificial ageing test, commercial films were also selected, one is a motion picture film, and four are photographic negatives (one sheet film, three 60mm film).

Model films

Cellulose nitrate

Cellulose nitrate filtration membranes from GE HEALTHCARE were used to prepare CN films.

Cellulose acetate model film

The preparation of DAC films was done by dissolving granules of the pure polymer (5% w/v) in acetone (95%) in order to obtain a relatively homogeneous film by pouring the solution on a glass cuvette and evaporating the solvent. The CA used was from SIGMA-ALDRICHT with M_n 50000(GPC) and 39.7 wt.% acetyl content. It was used acetone 99.6% . The film was cut into 4x4 cm samples.

Cellulose triacetate model film

The preparation of CTA films was done by dissolving granules of the pure polymer (5% w/v) in chloroform (95%) in order to obtain a relatively homogeneous film by pouring the solution on a glass cuvette and evaporating the solvent. The CTA granules are from are from SIGMA-ALDRICHT and have a solubility 0.1g in 10ml $CHCl_3$. The film was cut into 4x4 cm samples.

Commercial films with cellulose nitrate support

- Sheet film with format 13x18 cm. Expiring date indicated: 1944.
- Motion picture roll film, panchromatic, ISO 15. Expiring date indicated: 1950.
- Film A, medium format (60mm). Expiring date indicated: 1932.
- Film S, medium format (60mm), orthochromatic, non-curling. Expiring date indicated: 1933.
- Film F, medium format (60x90 mm), with anti-halation layer.

Photographic processing

Films were exposed through a transmission step-wedge (density range 0.5 – 3.05, 21 steps) to produce a range of black, white and grey tones with density increments of 0.16. The transmission step-wedge and the films were placed in contact and exposed to light for 30 s.

After exposure, the exposed films were developed. The processing solutions for sheet and roll films medium format the developer and fixer were:

Development with T-MAX[92] developer (1.4 v/v dilution in water)

Stop bath with acetic acid (1.10 v/v dilution in water)

Fixer solution (ILFORD RAPID FIXER[93]) (1.4 v/v dilution in water)

The processing solutions for motion picture film differed on the type of developer used, which was the developer D-96 (hydroquinone-based).

[92] The developing agent is hydroquinone-based.

[93] The fixing agent is ammonium thiosulphate.

The development was carried out at a temperature ~22 to 24^{0}C. The times for development ranged from 15 min (motion picture film), 11 to 6 min (sheet film and roll films).

5.7 Instruments and methods

5.7.1 Sampling

Samples from historical film-based negatives naturally aged were µ-sampled from accessible areas such as peripheric areas of the negatives (Fig. 5.2), for micro-Infrared and micro-Raman spectroscopy analysis. A prior test was performed to understand the spectral differences that could be found in different areas of one single negative. The test was performed in negatives with CN and CA supports. After µ-FTIR analysis of five samples taken from each negative it was concluded that there were different (and sometimes significative) spectral changes on each negative analysed. Therefore, for this work, it was decided to collect a sample from one single area of the negative to be examined.

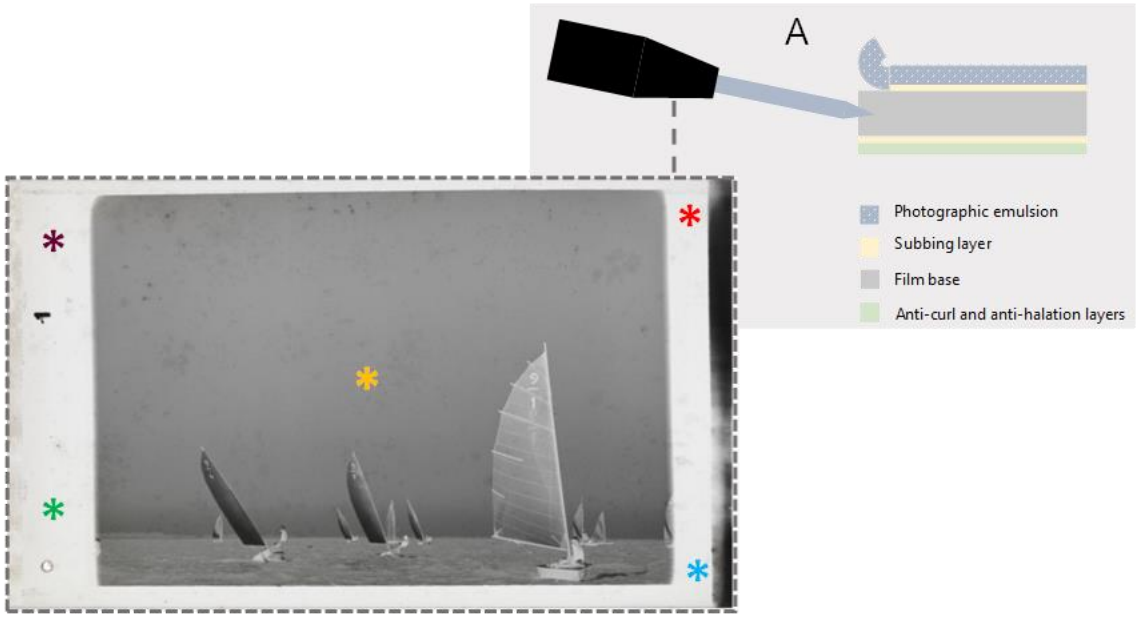


Figure 5.2 – Example of the methodology used for sampling (A) and pH and hardness measurements (*).

One sample was collected per each negative selected and per model film by using a *Ted Pella* micro tool, a scalpel under a Leica MZ16 stereomicroscope with a 7.1 to 115x zoom range, equipped with integrated Leica ICD digital camera and a Leica KL 1500 LCD external cold light source with two flexible optic fibre cables. To ensure an accurate characterization of the film support, the photographic emulsion, subbing layer and anti-curl layers were removed with micro-tools and a scalpel, under stereomicroscope.

The samples were individually stored between two concave glass slides, used as sample holders.

5.7.2 Artificial ageing

4x4 cm CN reference and commercial CN films were exposed to light (sensitized), chemically processed and analysed before and after artificial ageing. Unaged samples were used as control in all analyses. Relative results are obtained from artificial ageing, therefore by performing this ageing test it was intended to compare the degradation pathways of negatives with CN support and different formats, and to confirm the effectiveness of the pH and hardness measurements on this type of negatives. Moist heat artificial ageing was performed at 80^0C±0.5^0C and 90%±0.2% relative humidity (RH), for 168 hours in a FITOCLIMA 150 EDTU climate chamber. Samples were placed separately from each other on glass supports (Fig. 5.3).

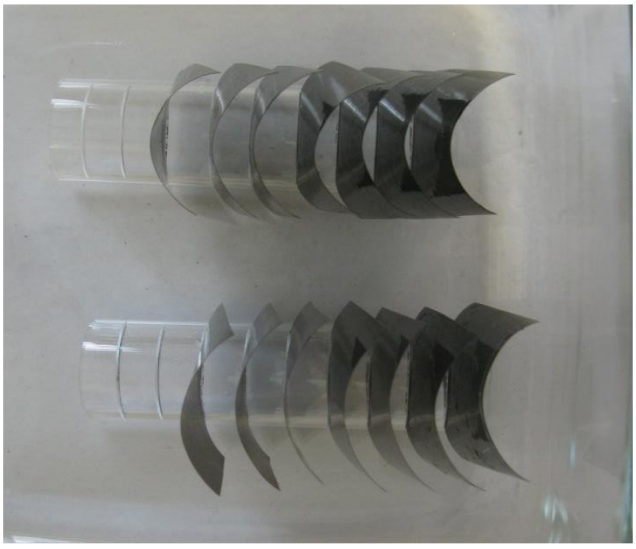


Figure 5.3 – Detail of commercial films placed on glass supports.

Before and after artificial ageing, the samples were kept at 22^0C ±2^0C, 40%±2% RH in a desiccator.

5.7.3 Colourimetry

Colour measurements were carried out with hand-held colourimeter Data Colour International® with a D65 Standard Illuminant and 10° Standard Observer, following the International Commission on Illuminant (CIE) colourimetry system. The CIE $L^*a^*b^*$ colourimetric space is defined according to three coordinates: L^*, a^* and b^*. L^* is referred to the level of lightness (0=black, 100=white); a^* is referred to the redness-greenness (red: $a^*>0$, green: $a^*<0$); and b^* to the yellowness-blueness (yellow: $b^*>0$, blue$^*<0$).

Samples were measured on top of 7 layers of Whatman#1 paper, using a transparent polyester sheet film template to position the colourimeter in the same spots for each measurement taken. The reported. L^*a^*b values for each negative are thus the average and standard deviation of 6 measurements performed in 4 different areas, in a total of 24.

5.7.4 Hardness

Samples hardness (Shore A) was measured with a *HP Durometer* (model HPSA, from Checkline Europe). For each sample the hardness and standard deviation (SD) values were determined as the average of five independent measurements.

Figure 5.4 – Overall view of HP Durometer.

5.7.5 pH

pH measurements were performed using a surface pH measurement method for paper, TAPPI 529 om-04 (TAPPI, 2009), using a *Unisense* pH/mV meter with *pH-500* microelectrode, with 400-800 µm external diameter, and a glass reference electrode with a 10µm external diameter. After testing it was established to use a drop of 0.02mL Millipore water (Fig. 5.4). The reported pH values for each negative is the average and standard deviation of 5 measurements. For the selected films from ECC collection, by request of the conservator responsible for the collection, the measurements were performed in the four corners of the object in order to avoid possible risks of damaging the objects.

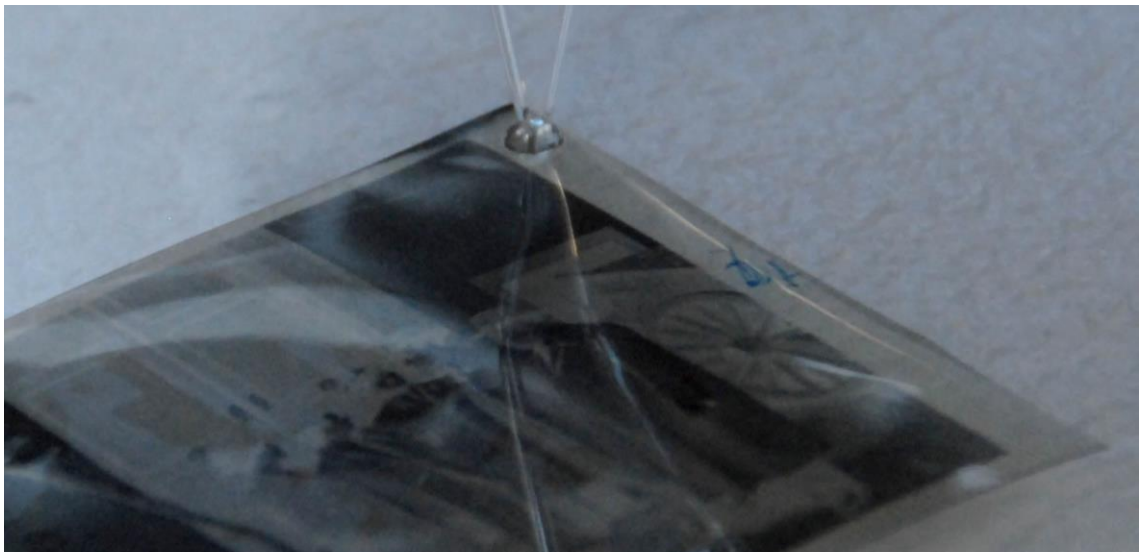


Figure 5.5 – Detail of pH measurement with micro-electrodes (potentiometric method).

5.7.6 µ-FTIR

Infrared (IR) spectra were acquired using a *Nicolet Nexus* spectrophotometer coupled to a *Continuum microscope* (15x objective) with a MCT-A detector cooled by liquid nitrogen. The analysis was performed on µ-samples previously compressed with a *Thermo* diamond anvil cell. IR spectra were collected in transmission mode from 4000 to 650 cm^{-1}, 128 scans and 4 cm^{-1} spectral resolution. Spectral analysis was performed using *Omnic E.S.P.* and *OriginPro 8* software and all spectra were baseline-corrected. CN spectra were normalised to CH absorption at ≈1374 cm^{-1} and CA spectra were normalized for C-O-C stretching (1051 cm^{-1}) (identified as the most stable absorption). CO_2 absorption at ca. 2300-2400 cm^{-1} was removed. The baseline correction was carried out as follows:

- Cellulose nitrate naturally aged and artificially aged film supports, at 4000, 3000, 2800, 1800, 1220, 930, 770, and 650 cm^{-1} absorption frequencies;

- Cellulose acetate naturally aged and artificially aged film supports, at 4000, 3000, 2800, 1900, 1680, 1340, 995, and 805 cm^{-1} absorption frequencies.

5.7.7 µ-Raman

Raman spectra were obtained from µ-samples from naturally aged samples from the collections studied and from films artificially aged, using a Horiba Jobin Yvon LabRam 3000 spectrometer, equipped with He-NE laser 17 mW operating at 632.8 nm and coupled to the Confocal Microscope with high stability Olympus BX 41. The laser beam was focused with an Olympus LMPlanFL N 50x or 100x, with a spot size of 2 µm. Collection time was 15-25 seconds and 20 to 30 scans; depending on the sample the laser power was varied with neutral density filters (optical densities: 0.3, 0.6 and 1.0 filters). Three

Raman spectra were collected on three independent points at the top of each sample. Raman data analysis was performed using *LabSpec 5* software and all spectra were baseline-corrected for the following wavenumbers:

Naturally aged CA-based negative, at 150, 320, 400, 520, 700, 860, 990, 1050, 1195, 1450 cm^{-1}.
Unaged CDA film, at 400, 860, 1050, 1600, 1800 cm^{-1}.

Naturally aged CN-based negative, at 375, 580, 980, 1190, 1490, 1600 cm^{-1}.

Unaged CN film, at 400, 860, 1050, 1600, 1800 cm^{-1}.

5.7.8 μ-EDXRF

Micro-energy dispersive X-ray fluorescence analyses were carried out using an *ArtTAX* spectrometer from Bruker, with a molybdenum (Mo) X-ray source, focusing polycapillary lens and electro-thermally cooled *xFlash* (Si drift) detector, with 170 eV resolution (Mn Kα). The accurate positioning system and polycapillary optics enable a small area of primary radiation (Ø~70 μm) at the sample. Elemental composition was obtained from the analysis of six independent spots (three transparent areas and three areas of the image), with a tube voltage of 40KV and a current intensity of 600 μA and live time 100s. Spectra are presented as acquired.

5.7.9 Scanning Electron Microscopy – Energy Dispersive Spectroscopy (SEM-EDS)

The morphology of the cross-sections of four film based-negatives was characterized by SEM-FIB using a *Carl Zeiss AURIGA* Cross Beam workstation instrument equipped with an *Oxford* X-ray Energy Dispersive Spectrometer. Mounted samples were analysed with a C coating. The experimental conditions of the image acquisition were 5 kV accelerating voltage, 20 μm of beam emission and 4.8 working distance. Elemental composition was obtained from the analysis of six independent spots (two on the emulsion layer, two on the film support, two on the anti-curl layer (see a cross-section of the film in Chapter 2).

5.7.10 Near-IR

Near infrared spectra were recorded on a Fourier-tranform NIR analyser (Antaris I, Thermonicolet, Madison, ThermoNicolet), equipped with a reflectance fiber optical probe, with Ø spot c. 8mm (SabIR, ThermoNicolet), and an indium-gallium-arsenide (InGaAs) detector. The equipment was controlled via the Result software package

(ThermoNicolet Industrial Solutions, Madison, USA) which enables the automated acquisition of the NIR spectra. The spectrum for each sample was recorded with a $4cm^{-1}$ resolution with an average of 64 scans over a wavenumber range between 4250 and 10,000 cm^{-1}. The measurements were performed in diffuse reflectance mode, using a fiber optical probe. Before each samples measurement, a background spectrum was performed inserting the probe into the fibre optical reference (Spectralon).

5.7.11 Statistical analysis

This approached was used for the assessment with pH and hardness, and μ-FTIR analysis of naturally aged samples through the Pearson coefficient. The statistical analysis was conducted by Statuistica v.8 software (Saftsoft Ibérica). Pearson correlation coefficient and significance differences were considered significant at a p-value below 0.05.

Chapter 6 – Case studies: unveiling the degradation of cellulose esters still film negatives from five Portuguese collections

Chapter 6 – Case studies: unveiling the degradation of cellulose esters still film negatives from five Portuguese collections

6.1 Preamble

In the former chapters the ephemeral nature of cellulose esters film-based negatives and risks associated to the decay of those photographic materials was emphasized. In Chapter 2, the external and internal degradation factors that contribute for the decay of these negatives were presented along with an explanation of the common mechanisms of degradation associated to both cellulose nitrate and cellulose acetate-based negatives. It became clear that the decay of these of materials is complex, sometimes assuming heterogeneous behaviours which are difficult to explain and challenging when it comes to detect the 'shift point' for autocatalytic decay.

In Chapter 3, a summary of investigations carried out to study the decay of cellulose esters was presented. In this summary the methodologies and analytical techniques used to identify and assess the film support of still and motion picture are presented, showing the assorted techniques used, and the findings accomplished. In this same chapter, aiming at complementing the information about identification and assessment, due to the similarities between photographic and cinematographic film, references to identification, assessment and preservation of the later were included. The methods and products developed for simple identification and assessment of still and motion film decay (e.g. AD-STRIPS) were not forgotten, being given detailed information about the advantages and disadvantages of each method and product.

As previously described in Chapter 1, the main focus of this study are Portuguese collections. To have a panorama of the amount, type and condition of plastic negatives collections held by Portuguese institutions, a questionnaire was carried out. In this questionnaire the participants were also inquired about the methods used to identify and assess the condition of plastic negatives, and preservation actions implemented in the institutions. The results of the questionnaire presented in Chapter 4 confirm that the reality of Portuguese archives is identical to other international archives, e.g. the lack of conservators to carry out the actions necessary for the safeguard of large film collections is clear. More important, the results reveal that the identification and evaluation of the preservation condition of film-based negatives mainly rely on destructive field tests (e.g. density test) and macro assessment, being odour, the main sign of degradation used for assessment of the negatives. This finding is alarming considering that it indicates that conservators are often exposed to toxic solvents (e.g. trichlorethylene), acetic and nitric acid, a situation that may degenerate in health problems. Given the current situation, this study is found a priority. It aims to be a starting point for an in-depth knowledge of film-based negatives collections resulting from the work of Portuguese photographers, in order to survey the materials present in the collections and to systematize the data obtained for the definition of an identification and evaluation methodology that fits the

reality found in the Portuguese archives, and to others caretakers that face similar realities.

This chapter discloses the identification and assessment of the collections. The results obtained are presented in two main sections, the macro assessment and the molecular assessment of the negatives examined. For start, the macro assessment (MA) results obtained during the observation and selection of the negatives are presented per collection. The macro assessment contemplated the visuals signs and odour detected per negative selected. In this section a brief contextualization of the past storage and conservation and preservation interventions is performed to explain either the selection performed as well as the current preservation condition of the negatives selected. Then, the amount and condition of the negatives selected is described, as well as original brand marks and notch codes found. At the end of this section, a compilation of the macro assessment results obtained is delivered, launching the topics for the molecular assessment. Following this first section, the molecular condition of the selected negatives is presented based on IR spectroscopy, pH and hardness (Shore A) results. The identification of plasticizers carried out by Raman spectroscopy is also presented. Additionally, since assorted hues were visually perceived on negatives from ECC and SP collections, micro-EDXRF and SEM-EDS analysis were carried out to identify the chemical compounds present in the image layer. The results obtained are shown along with suggestions of the possible corrective treatments performed by the photographers, pointing out for possible storage methods and image treatments performed in colonial photography. A discussion concerning effective and non-effective relationships between molecular data and the visual assessment is also presented, giving a new insight into novel methods for identifying and assessing cellulose nitrate and cellulose acetate-based negatives.
To conclude, the results of macro assessment and molecular assessment of the overall collections are discussed and compared, being disclosed the findings accomplished with this work.

6.2 Macro assessment of the selected case studies

In this section the macro assessment results accomplished for each collection are presented. An extensive description of embossed marks, notch codes and condition evaluation performed by macro assessment of the case studies selected from each collection are disclosed. An overall comparison of the results accomplished for all sets of case studies will be performed, narrowing the identification and assessment issues and variables found in this study. By comparison, the data presented for ECC and SP collections is broader, reflecting the large quantity of case studies selected, and also the variety of issues found within each collection. The results obtained in the macro assessment of ECC collection, will be the first to be presented, launching the discussion

about the identification and assessment of nitrate-based negatives. Since the set of case studies from ECC, DGEMN and MN collections were previously identified as cellulose nitrate-based negatives, it was decided to start to present those collections.
Due to the lack of previous identification of the specimens and prediction of the presence of assorted types of film-based negatives, the data gathered during SP and SN collections macro assessment were presented at the end of this section.

6.2.1 Elmano Cunha e Costa collection

The overall exceptional condition of ECC collection was reported by the conservators who, in 2000's, have performed the survey, identification and conservation intervention. Given the quantities of film-based negatives presented in this collection (total of 8718 specimens), the conservators decided to carry out the identification of case studies randomly selected, confirming (by density tests) that all specimens tested have a CN base. The identification results were taken in consideration since this is one of the common field tests used by caretakers[94]. Thus, the selection of the case studies relied firstly on the identification previously performed, followed by the detection of identification marks (edge printing and notch codes) and visual signs that allowed to perform a first level of identification and assessment of the negatives. For this study 99 film-based negatives were selected from the ECC collection.
In the overall collection, one single negative with edge printing (brand and film type) and notch code, was found (Fig. 6.1, red box). With the designation 'Nitrate - KODAK' and a 'V' shaped notch code commonly associated nitrate supports from Kodak, in this case a straightforward identification was made. Since these evidences (edge printing and notch code) were found only in one negative, it was questioned if this photographic negative is an 'original' or a 'duplicate'? It is important to remember that Cunha e Costa did mentioned to have made two negatives from the same subject. However, duplicates were never found. Additionally, the financial difficulties reported by Cunha e Costa led to think that he might not had the money to purchase film and therefore, he may not have made two negatives from the same scene. It was thus considered that beside the negative with the notch code, the remaining film-based negatives are the originals. In a second step, the assignment of a period of production was tried by comparing the notch code with the extensive list of references available in the literature (Lester 1946; Lester and John S. Carrol 1956; Horvath 1987; Pavão 1997; Fischer 2012). Apparently, this case study corresponds to a 'Kodalith Pan' film, produced between 1942 and 1960[95]. Given the period of production of this type of film, it is suggested that this case study is a duplicate but more research will have to be done to support any attributions.

[94] The identification methods were already discussed in Chapter 3 and Chapter 4.
[95] David Horvath's Kodak Notch Reference 33 B (Horvath 1987, pp. 56, 66). In the list of references given by Horvat, another Kodak notch reference, 35 B, similar to 33 B was found (Horvath 1987, pp. 56, 67).

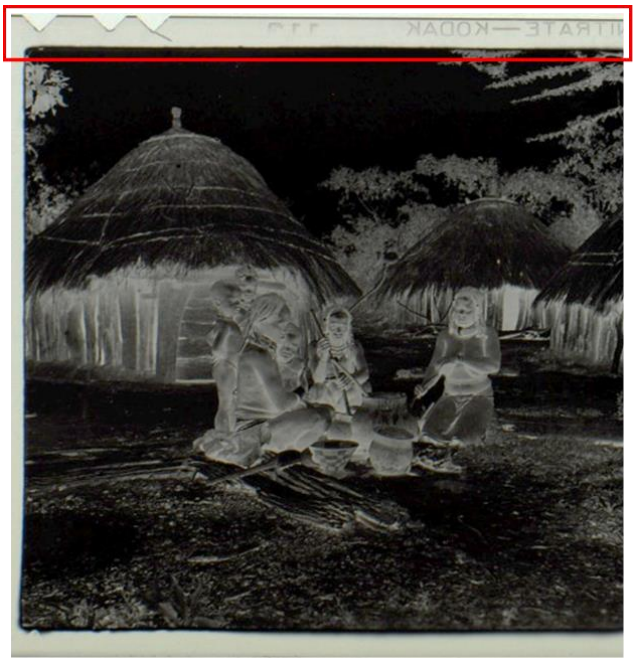


Figure 6.1 – Case study from ECC collection (catalog number ECC 4461). Top left: 'V' shaped notch code. Top right: embossed designations 'Nitrate' and 'Kodak'. ©AHU-DGLAB/Credit: Élia Roldão.

Beside that single case, the selection of negatives from ECC collection relied mostly in the macro assessment of their condition, following the condition grades previously described[96]. In Fig. 6.2, a list of the common degradation signs observed in the negatives selected from ECC collection are presented.

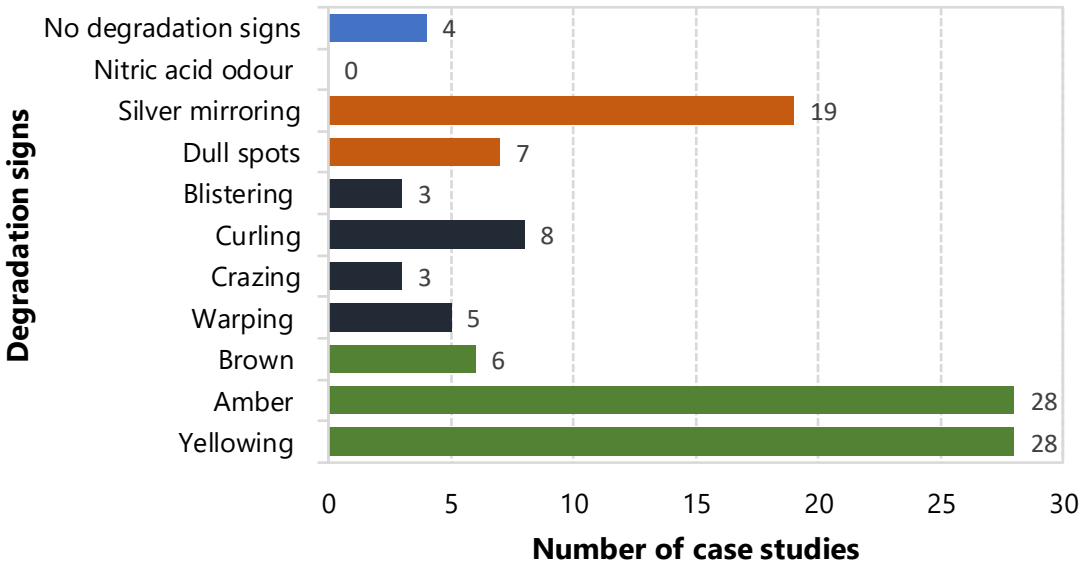


Figure 6.2.- Degradation signs macro assessed in the case studies selected from ECC collection. Lack of degradation signs (blue bar); silver mirroring and dull spots (orange bar); change in shape and cohesion (deep blue bars); discoloration (green bars).

[96] In the framework of this study a Table 5.1 was designed aiming to describe the macro degradation signs for each condition grade based on which the macro assessment is supported.

As shown in Fig. 6.2, discoloration (general yellowing, amber and brown tonalities) and *silver mirroring* (oxidation of the silver image) are the main degradation signs found in the case studies from ECC collection. The occurrence of general yellowing, amber and brownish hues in cellulose nitrate-based negatives are correlated with chemical decay of the support layer[97] (Lavédrine 2000; Valverde 2005; Fischer 2012). Taking this into consideration, discoloration supported the selection and visual assessment carried out.
In opposition to what was expected for a film collection from the 1930's, odours associated with chemical decay of the film support was not detected. Remarkably, four case studies with no signs of degradation were found, considered 'good as new'. In Fig. 6.3, examples of case studies considered 'good as new' (Fig. 6.3 a) and degraded (with brown discoloration) (Fig. 6.3 b) are presented.

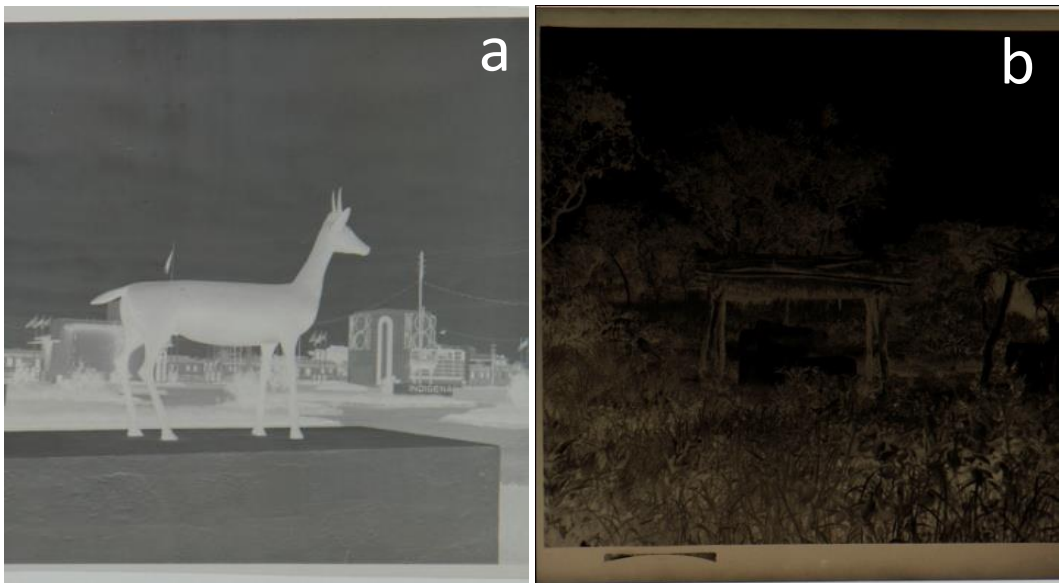


Figure 6.3 – Case studies from the ECC collection, (a) negative ECC 1, with no discolouration; (b) negative ECC 631, with brown discolouration. ©AHU-DGLAB/Credit: Élia Roldão.

Additionally, dull spots, blistering, crazing, curling and warping were visually detected in a minor number of case studies (Fig. 6.2). Occasionally, in a reduced quantity of case studies (total of eleven) it was observed that beside these minor signs of degradation (dull spots, blistering and crazing) the specimens also showed brown hue (discoloration). In Fig. 6.4 (a to d) details of degradation signs are shown.

[97] For more information see Chapter 3, Table 3.4, pages 80-81.

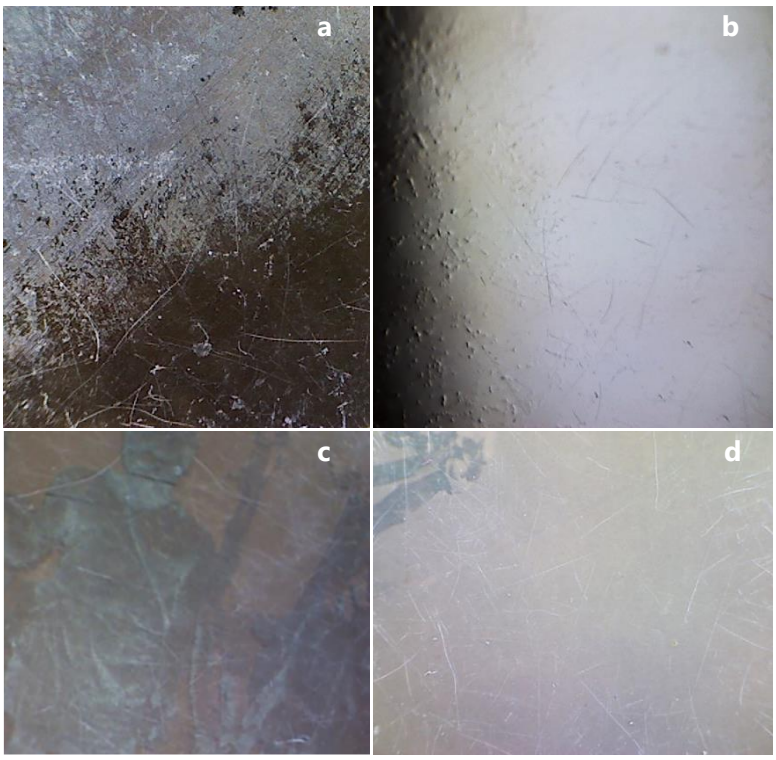


Figure 6.4 – Details of degradation signs observed in case studies from ECC collection: (a) dull spot, negative ECC 1256; (b) blistering, negative ECC 2416; (c) silver mirroring, negative ECC 7774; (d) crazing, negative ECC 5711.

Furthermore, distinct hues on the image layer were visually perceived. Visually, the hues were only detected in the image layer, reinforcing the possibility of the tonalities found being related with chemical treatments of the image, and distinguishing them from discoloration resulting from chemical decay (e.g. general yellowing or tonalities associated with regeneration of the anti-halation dyes due to pH changes). Pale pink, intense yellow, red-brownish, orange-brownish or greenish hues were visually identified on the image layer of the case studies selected from ECC collection. The quantity of case studies with assorted hues is presented in Fig. 6.5.

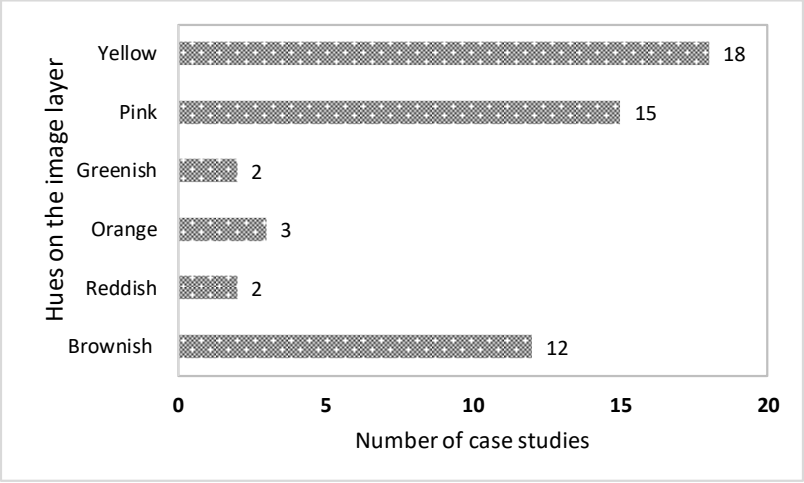


Figure 6.5 – Hues found on the image layer of case studies selected from ECC collection.

As previously presented[98], commonly photographers performed chemical corrective treatments to improve the density and contrast of b/w images. From those chemical treatments the appearance of assorted hues (general or stains) may occur (Eaton et al. 1985). Based on the hues and its incidence, those are considered markers of the practice of different corrective treatments by Cunha e Costa. Moreover, this suggestion is also supported by the invoices of purchase of mercury and iodine found in the historical documentation associated with the ECC collection. Moreover, red ink masks were observed in two case studies from ECC collection.

Based on the incidence and location of the degradation signs aforementioned, case studies from the ECC collection were macro assessed, and the condition was evaluated in agreement with the degradation chart (Table 5.1). The case studies selected show conservation conditions ranging between 1 (Very Good) to 4 (Poor) (19 case studies) (Fig. 6.6).

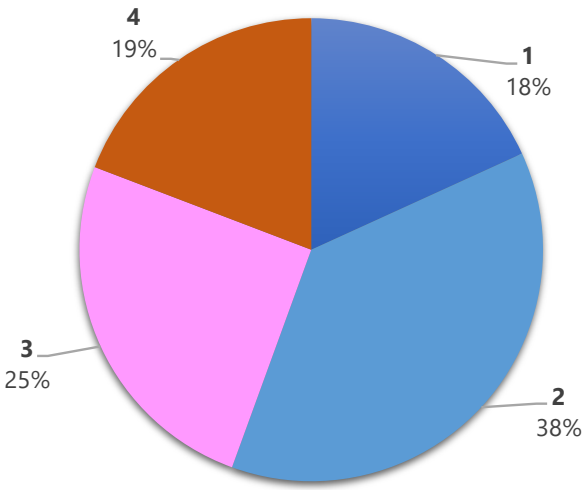


Figure 6.6 – Percentage of case studies according to condition 1 to 4 (**bold**, evaluated by visual assessment).

According to the visual assessment carried out (Fig. 6.6), overall, the collection was overall considered in Good to Fair condition.

6.2.2 Macro assessment of case studies from DGEMN collection

Given the cold storage practice implemented in DGEMN archive, the selection of the case studies for this work was restricted to two set of plastic negatives (circa 600 negatives previously identified as cellulose nitrate-based). For identification the density test was formerly carried out by the institution conservators. Comparatively with the ECC collection, in the DGEMN collection it was possible to assess film-based negatives with assorted formats, brands, and notch codes.

[98] See Chapter 2, section 2.4, and Appendix I.

From the total set of negatives available, 49 were selected, with formats ranging from 35mm (5 case studies), 6x6 cm (13 case studies), 9x12 cm (11 case studies), 10x15 cm and 13x18 cm (13 case studies) and 18x24 cm (7 case studies). Regarding the dates of production of the case studies, except for two (with the dates '1949' and '1950' written on the edge of the negative), no information was found[99].

About film brands and notch codes, different marks were found. For instance, all case studies with a 35mm format are from Agfa. Concerning case studies with formats 9x12 cm to 18x14 cm, the brands Ferrania and Eastman Kodak were respectively identified in five negatives, respectively. However, as also observed for the ECC collection, for negatives with 60mm format, no edge printing or notch codes were found. With regard to notch codes, eleven case studies have these marks. In Fig. 6.7, the notch codes found in the set of case studies from DGEMN collection are presented. Most of the notch codes have a 'V' shape (Fig. 6.7a to f), while two have a 'U' shape (Fig. 6.7g and h) and square shape (Fig. 6.7i).

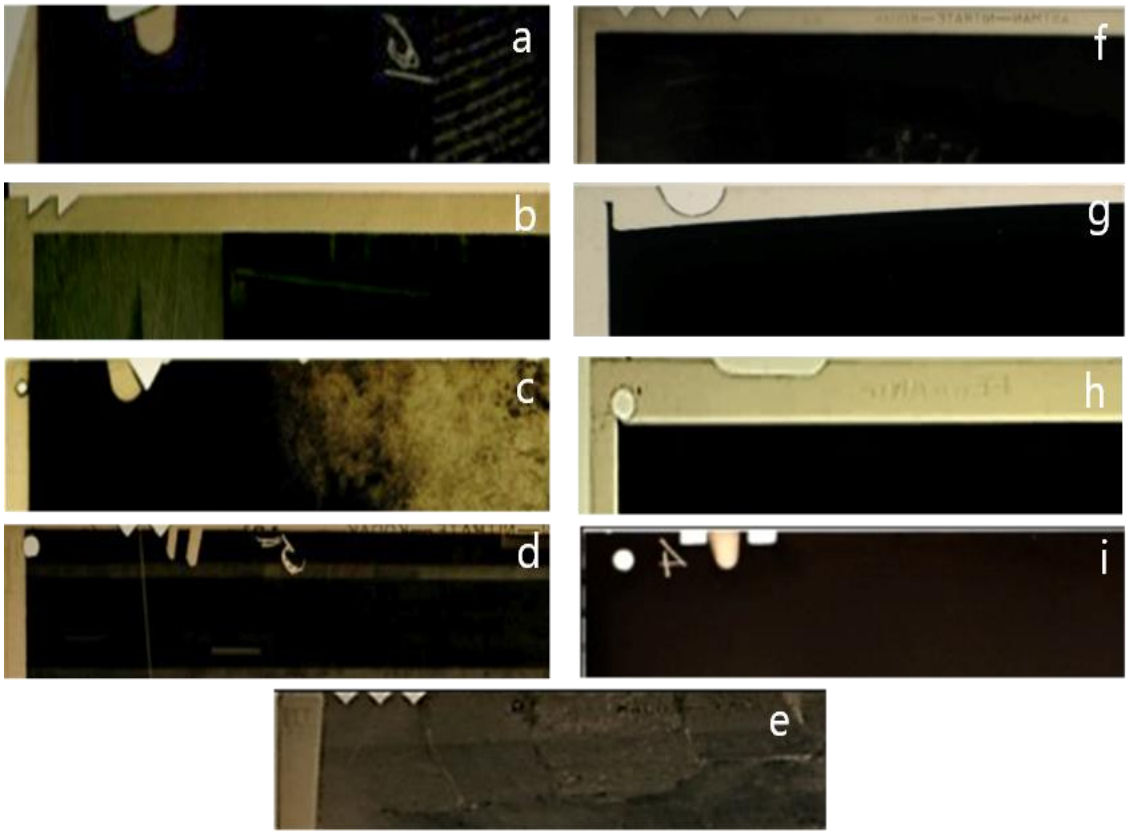


Figure 6.7 – Examples of the notch codes identified in case studies from DGEMN collection, with 'V' shape (a to f), 'U' shape (g and h), and square shape (i).

In some cases, notch code, film type and brand references were found. As example, in Fig. 6.7d, e and f, all with a 'V' notch code, the 'Eastman Nitrate Kodak' embossed mark was observed. This data correspond to references found in the literature (Valverde 2005;

[99] According to information disclosed in the conservation intervention report, the original enclosures of these specimens were completely degraded and then disposed of. Therefore, no dating information is available.

Fischer 2012). A similar correlation, but this time between a notch code with a 'broad U' shape and Ferrania brand was found (Fig. 6.7 h).
Beside these marks, degradation signs were used as markers for identification and assessment of the condition of the selected case studies. In Fig. 6.8 a summary of the results obtained with macro assessment are presented.

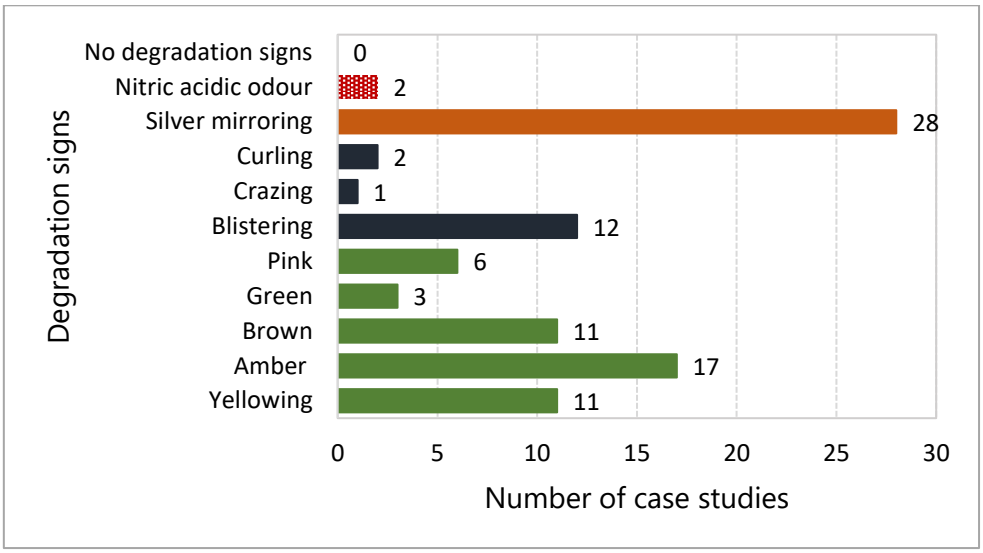


Figure 6.8.- Degradation signs macro assessed in the case studies selected from DGEMN collection. Degradation signs: nitric acid odour (red bar), silver mirroring (orange bar), change in shape and cohesion (deep blue bars), discoloration (green bars).

According to the macro assessment results, for two case studies from DGEMN collection an acidic odour was noticed which, due to previous identification of the films based, was associated with nitric acid odour (Fig. 6.8.). Comparatively with case studies from ECC collection, blistering was visually detected in a larger number of case studies from DGEMN collection.
As for ECC collection, in general, discoloration and silver mirroring are the major degradation signs observed.
Besides yellowing to dark brown discolorations, green and magenta hues were also visually perceived. As previously explained[100], commonly the magenta hue is associated with cellulose acetate decay, resulting from acidification of the support and regeneration of the anti-halo dyes. Given that association between cellulose acetate-base and magenta hue, the identification accomplished with the floating test was questioned.

In Figure 6.9, a case study with discoloration (dark brown) from the DGEMN collection is presented.

[100] See Chapter 2, page 63 and 64.

Figure 6.9 – Overall discoloration (dark brown) of a case study (catalogue nº DGEMN 17_8) from DGEMN collection. ©SIPA-DGPC /Credit: Élia Roldão.

Additionally, local discoloration and loss of anti-curling layers were observed in two case studies. Figure 6.10. (right side of the image) depicts a detail of such occurrences in one of the case studies. As it is known, discoloration results from the formation of chromophores, e.g. nitrate groups, that will selectively absorb visible light and render a colour hue.

Figure 6.10 – Detail of local discoloration (intensive yellow hue) and loss of the anti-curl layer (right side of the image). Case study 15_127 from DGEMN collection. © DGPC-SIPA/ credits Élia Roldão.

For some decades, this photographic collection had been stored in rooms without environmental control (temperature, relative humidity or ventilation). Thus, given the intensity and shape of the changes observed it is suggested that prolonged exposure to high relative humidity or contact with water might be the cause for such an uneven decay of the specimens.

The selection of the case studies was supported on the criteria described above. Regarding the presence and extension of the degradation signs observed, the condition of the case studies was performed. In Fig. 6.11, the overall condition of the case studies selected is shown, disclosing the amount of case studies according to condition.

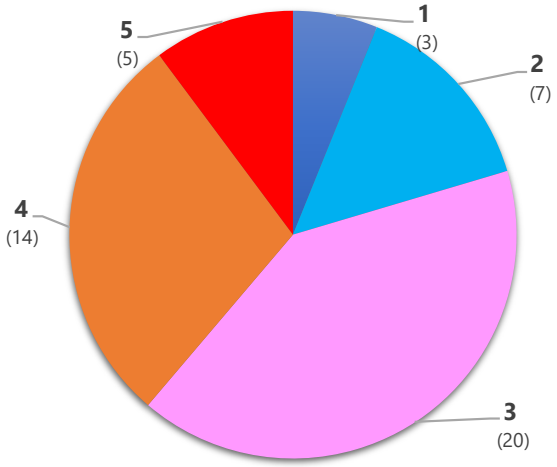


Figure 6.11 - Number of case studies (between parenthesis) according to condition 1 to 5 (**bold;** preservation condition performed by visual assessment).

It was noticed that the cases of studies classified as severely degraded (condition 5) have the formats 9x12 cm and 13x18 cm. Despite the signs of advanced degradation indicated, no acidic odours could be detected in the case studies.

6.2.3 Macro assessment of the case studies from Mario Novais collection

As described above, in the ECC and DGEMN collections, case studies with different production frameworks and assorted formats, embossed identification marks and condition were found. However, beside two case studies from DGEMN collection that showed loss of emulsion layer and brown hue, none of the cases studies selected shown the typical signs of degradation associated with cellulose nitrate-based negatives (e.g. negatives glued to each other, brittleness, noxious nitric acid odour, loss of the image layer)[101]. After contacting the AHU, SIPA and ADF archives with no success, examples of specimens showing the aforementioned degradation signs were reported by the conservators of Biblioteca de Arte archive, from FCG. During the conservation

[101] See Chapter 5, Table 5.1.

intervention of the Mario Novais (MN) collection, this set of cellulose nitrate-based negatives was separated from the rest of the collection, enclosed with barrier foil[102] and frozen. In Fig. 6.12, a detail of the set of negatives from MN collection is shown, where brittleness, marked yellowing-brownish hue, and lack of the image layer are perceptible, together with a congealed semi-crystalline deposit on their surface.

Figure 6.12 – Detail of the set of nitrate-based negatives completely degraded from MN collection. © BA-FCG/ credits Élia Roldão.

In opposition to the case studies from the other collection selected for this study, after opening the enclosure Marvealseal® bag a noxious odour and extreme brittleness were perceived. The strong adhesion between specimens prevented to count them. Nevertheless, it was possible to measure the negatives (set of glued negatives) and confirm that these are large format negatives with a 18x24 cm^2 format.
The degradation signs perceived allowed to conclude that within the collections and case studies already surveyed, there was not a single case that could be compared with the MN collection. Based on the surveys carried out in this work, the MN case study was considered to exemplify the severe degradation of cellulose nitrated-based negatives, classified as within condition 5 (see Chapter 5, Table 5.1).

6.2.4 Macro assessment of the case studies from San Payo collection

The motives for selection of the San Payo (SP) collection have already been presented. In the beginning of this study an extensive survey of the collection was being carried out by the archivist and conservators of the ADF archive. In the framework of this study it was decided to, as much as possible, to carry out, as much as possible, the selection of

[102] The barrier foil consists on an aluminium shielding (moisture barrier) and polyethylene film layers commonly used to enclosure the cellulose nitrate and cellulose acetate-based negatives which are going to be frozen or stored in cold storage facilities.

case studies along with the survey that was being performed. Figure 6.13 depicts the original boxes in which the plastic negatives were stored.

Figure 6.13 – Overall view of the original boxes where the case studies from San Payo collection were stored. © DGPC-ADF/ credits José Paulo Ruas.

From the circa 12 300 plastic negatives surveyed, 190 case studies were selected. In this collection, assorted formats, brands, and notch codes were found. Regarding formats, the quantity of case studies selected per format are presented in Table 6.1. Additionally, the brands found per set of negatives selected are also presented.

Table 6.1 Film formats, quantities and brands found in San Payo collection

Film formats	Collection (%)	Case studies (quantity)	Brands	Case studies per brand (%)
35 and 60 mm	21	42	Ilford Kodak 'Unknown'	5 17 78
9x12 cm	74	127	Kodak 'Unknown'	40 60
10x15 cm,13x18 cm and 18x24 cm [103]	5	21	Kodak 'Unknown'	71 29

[103] In this collection, film-based negatives with 18x24 cm were firstly separated from the remaining collection due to the degradation signs observed, which were associated with the decay of cellulose nitrate-based negatives. Therefore, in the framework of this study those plastic negatives were not saw.

As shown in Table 6.1, in San Payo collection the incidence of specimens per format varied. By comparing the percentages of each format found in the collection, it is possible to conclude that San Payo used sheet film (9x12, 10x15 and 13x18 cm^2 film-based negatives) to perform is professional work. Comparativelly, a minor percentage of specimens with 35 (a six frame strip) and 60 mm formats was surveyed, in which the topics found were correlated with sport events or photographs of San Payo's familiy. Thus, in part the case studies selected from San Payo collection reflect the incidence of the formats and topics found in the collection, confirming the representativeness of his portraiture work in the overall collection (Table 6.1).

A straighforward identification of the Ilford and Kodak brands was suported by internal references (brand embossed on the edge of the film). Ilford films were only present in the set of 60mm format films, as well Kodak films that were also present in the 60mm and 35 mm formats. However, for a large percentage of case studies of all types of formats no producer or brand identification was found. In this study, in order to facilitate the discussion of the results, it was decided to designate those films without producer/brand references as 'Unknown' (Table 6.1). Regarding notch codes, a total 33 types of notch codes with 'U', 'V', 'square' and 'wide divot' shapes (alone or combined) were observed in sheet films. The majoraty of the 'Unknown' case studies have notch codes with a 'U' (68 case studies) or a 'square' (11 case studies) shapes. Moreover, a straigtforward identification of the film base was possible to accomplish for the case studies that have notch codes with 'square' and 'V' shapes (alone or combined) along with 'Safety Kodak' reference embossed. For case studies with notch codes but 'Unknown' producer/brand, in order to obtain possible production dates and identification of the manufactures, the notch codes were compared with Horvath's, Pavão's and Lester's lists. By doing so, it was possible to conclude that there are similarities and minor differences between notch codes used by different producers, a fact that difficults the correlation of those marks with dates and producers. One of the possible justifications for the appropriation and use of notch codes by different producers may be related with the merged work of entreprises such as Agfa-Ansco. In fact, when looking to the notch code lists found in the literature and presented (see Appendix II), it was found that Agfa is not listed. However, by taking into consideration Horvath's extensive survey of notch codes, the marks associated with Ansco are also related with Agfa. Nevertheless, there are still lacking more elements to support this possible relationship. At this stage, due to the lack of conclusive results, it was chosen to present the variety of the notch codes found in SP collection along with the identification of the film supports performed by FTIR analysis at the end of this chapter.

Beside internal evidences, the selection of the case studies also relied on the condition of the specimens. The condition evaluation followed the criteria described in Table 5.1. In Fig. 6.14 (a) and (b), two examples of case studies in conditions 1 and 5, respectively, are presented.

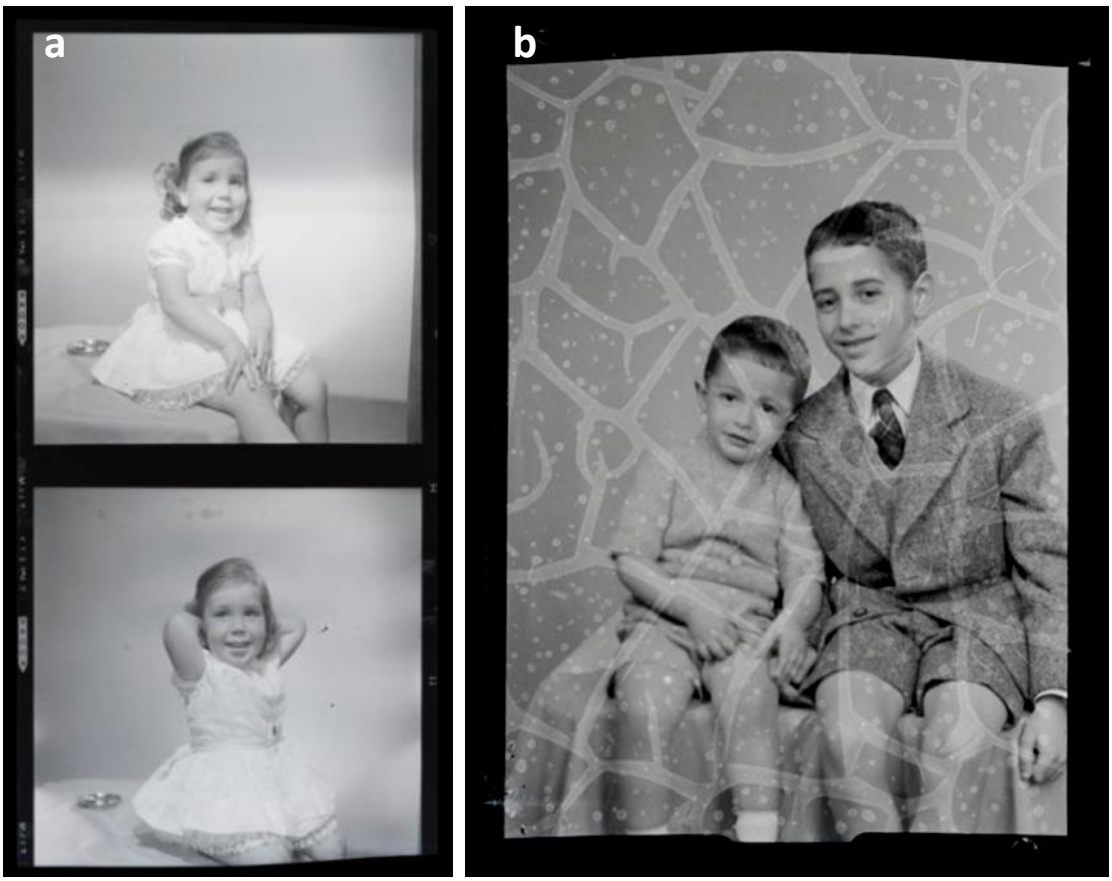


Figure 6.14 – Two case studies from San Payo collection in conservation conditions 1 (a) and 5 (b). © DGPC-ADF/ Credit: Luisa Oliveira.

Figure 6.15, amount of type degradation signs observed per case studies selected from SP collection is presented.

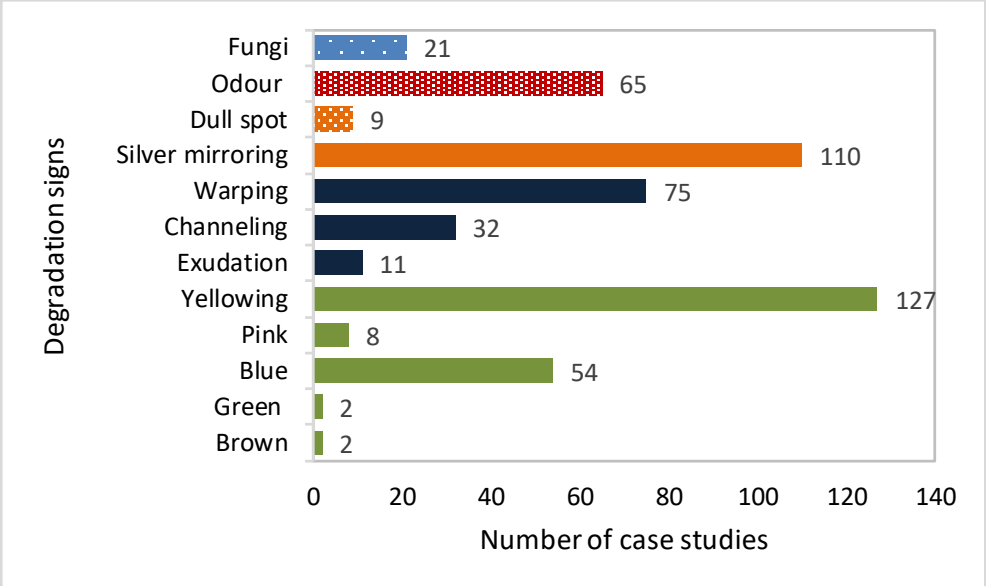


Figure 6.15- Degradation signs visually assessed on the case studies selected from SP collection: fungi (blue bar), acetic acid odour (red bar), silver mirroring and dull spots (orange bars), change in shape and cohesion (deep blue bars), discoloration (green bars).

During the observation an intense acetic acid odour was perceived. Due to the lack of individual enclosures, it was difficult to distinguish the intensity of acidic odour between the selected negatives; in fact, it seemed that all those were contaminated by that smell. To improve the assessment and perform an accurate evaluation of each negative, the plastic negatives were placed on a table for three hours (with ventilation), allowing to release part of the vinegar smell. Then, the evaluation of the odour was carried out and, as shown in Fig. 6.15, sixty-five specimens had a typical odour indicating the chemical decay of cellulose acetate-based negatives. Also associated with the vinegar syndrome, warping, channelling and plasticizers exudation were observed. Additionally, dull spots were also detected, which are also related with plasticizers migration (Fig. 6.15).

Associated with changes on the image layer, silver mirroring was observed in a large amount of case studies from SP collection, that might have been caused by the content of acidic gases trapped inside the original storage boxes or due to long-term exposure to high relative humidity. Possibly caused by long-term exposure to high relative humidity, fungi were detected mostly on the edges of the back layer (anti-curling) of the negative.

Regarding discoloration, assorted tonalities were observed, covering the overall surface of the specimen or appearing only as stains on the edge or on the centre of the back layer of the negative. Overall yellowing and blue tonalities were the most common hues visually perceived, followed by pink, green and brown tonalities, respectively (Fig. 6.15). Visually, the yellowing and brown tonalities seemed to be associated with the decay of the film support, while blue, pink and green tonalities were observed on the back of the negatives, on the anti-curling layer. Yellowing and pink tonalities were detected mostly on films with notch codes with a ‘square’ and ‘wide divot’ shapes, while blue and brown tonalities were perceived on case studies with notch codes with ‘U’ and ‘V’ shapes.

Figure 6.16 (a) and (b) depicts overall and local incidences of blue tonality, respectively, on two case studies from SP collection.

Figure 6.16 – Case studies with blue tonality in the overall surface of the case study (a), and as a local stain in the centre (b) both in the back of the negative. © DGPC-ADF/ Credit: Luisa Oliveira.

References to the used of blue anti-halation dyes by Agfa/Ansco were found in the literature (Horvath 1987, 11; Reilly 1993, 12). By crossing this information with the previous discussion about the use of notch code with a 'U' shape by Agfa/Ansco, and supported by Horvath (1987, 11) and Reilly (1993, 12) works, it is possible to suggest that the case studies from SP collection with blue tonalities and notch code with 'U' shape are from Agfa (or Agfa Ansco). This fact became of extreme importance since, from the overall set of specimens selected from SP collection, the case studies with blue hue and 'U' shape notch were, visually, the most degraded. This results are consistent with survey reports carried out by Horvath, in which the fact of Agfa/Ansco having produced cellulose diacetate-based negatives until 1955 is emphasized (Horvath 1987, 6,32). As previously said[104], cellulose diacetate is chemically more unstable than cellulose triacetate and cellulose acetate butyrate. Thus, cellulose diacetate-based negatives are known for their decay and potential risk of contaminate film collections, demanding accurate identification and close monitorization.

Once the generation of blue, pink and green hues on the anti-halation layer results from one the biological contamination and acid products resulting from the chemical decay of the film base (Reilly 1993, 12), case studies showing this degradation signs were selected in order to assess the pH of those specimens and correlate the pH values obtained with the molecular assessment carried out by FTIR spectroscopy analysis. In this way, it was aimed to, based on accurate analytical techniques, identifying trends on the

[104] See in Chapter 2, section 2.5.2 pages 61 – 64.

decay of cellulose ester film-based negatives that could allow to establish priorities that will support the definition and implementation of preservation strategies. Moreover, it was observed a relationship between plasticizers exudation (formation of crystals on the surface of the plastic negatives), the existence of blue hues and the notch code with 'U' shape. This particular set of case studies with these visual signs of degradation and notch code is, comparatively with the remaining case studies, representative of the cellulose acetate-based negatives severely degraded.

Regarding hues, pink and bluish tonalities were visually perceived on the image layer of three case studies from SP collection. In Fig. 6.17, an example of one of them with a pink tonality of the image layer is presented.

Figure 6.17 - Case study from SP collection (catalogue number SP 716) with pink tonality on the image layer. © DGPC-ADF/ Credit: Luisa Oliveira.

Despite of the lack of historical documentation in which the developing procedures carried out by San Payo were described, based on the visual assessment of these case studies it is suggested that the photographer performed corrective chemical treatments of the image. To confirm the causes of the hues found, µ-EDXRF analysis was carried out confirming the presence of chemical compounds used. The results obtained are presented in the next section. Moreover, it was also observed that beside the chemical corrective treatments, San Payo also employed red and green inks to mask the images, being found in three case studies.

Also as a consequence of the observations performed, it was concluded that the cellulose ester film-based negatives show assorted chemical and physical behaviours according to their formats. Thus, it was chosen to summarise the results obtained according to the formats surveyd. Figure 6. 18 a,b and c depict case studies condition grade according to

small and medium (35mm and 60mm) (6.18a) and sheet films with 9x12 cm (6.18b) and 10x15 and 13x18 cm (6.18c) formats and brands.

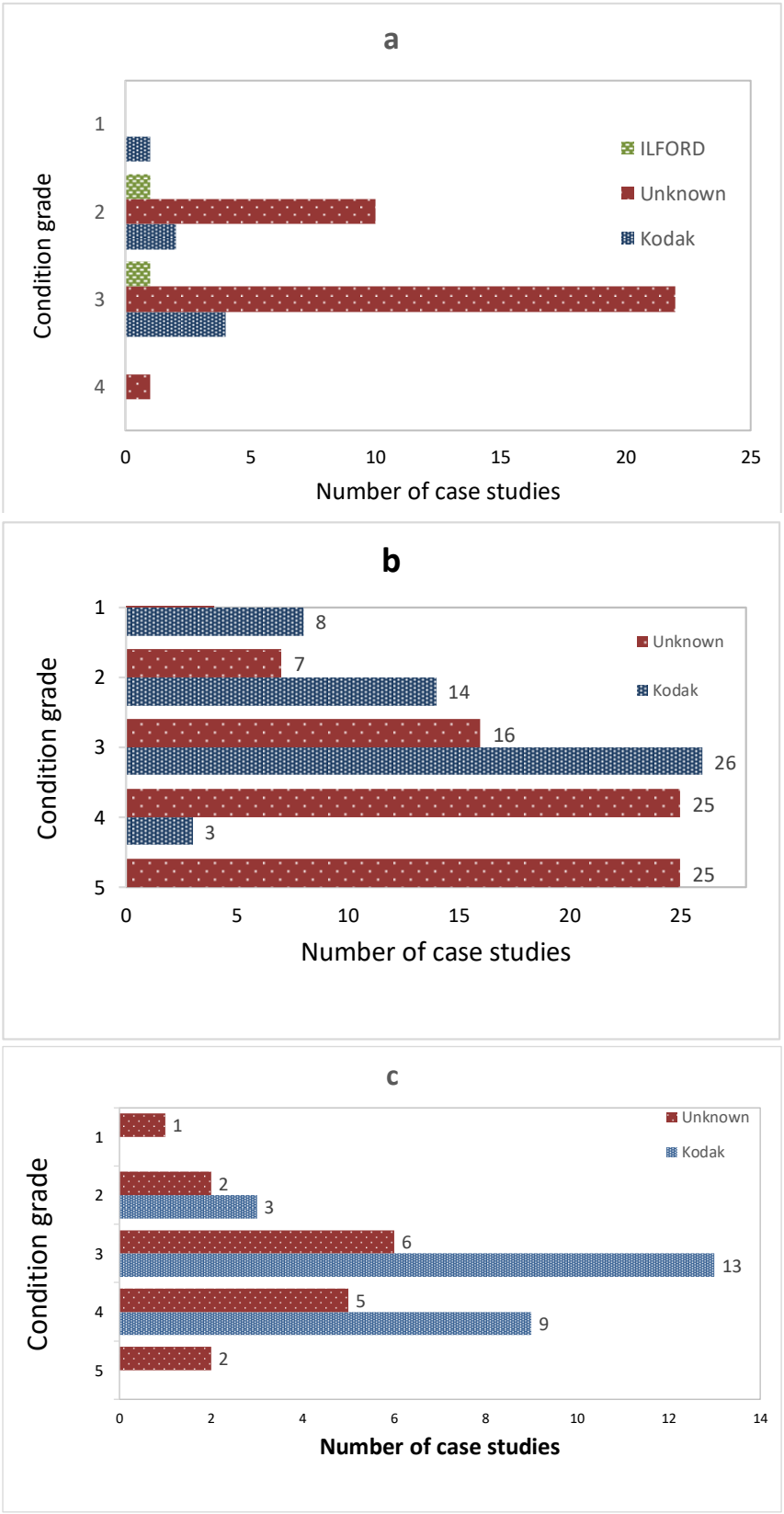


Figure 6.18 – Preservation condition (1 to 5) of the case studies selected from San Payo collection, according to formats and brands. Formats: 135mm, and 120 to 620mm (a), 9x12 cm (b) and 10x15 and 13x18 cm (c). Brands: Ilford (green), Unknown (red), Kodak (blue).

As presented in Fig. 6.18a, according to visual assessment, the majoraty of the case studies with 35 and 60mm are in conditions 2 (Good) and 3 (Fair). Comparativelly, a higher quantity of the negatives in conditions 3, 4 and 5 (Fair to Severe) were found in the set of specimens with 9x12 cm format. As the results show, the amount of selected samples with 9x12 cm format in conditions 4 and 5 (Poor and Severe) are from an Unknown producer, while negatives from Kodak represent the specimens in 1, 2 and 3 (Good to Fair) condition (Fig. 6.18b). Regarding sheet films with 10x15 and 13x18 cm formats, given the large percentage of case studies with Kodak brand within this set, Fig. 6.18c reflects that representativeness in the distribution of those speciments per condition. Moreover, discoloration (blue, pink and green hues on the anti-halation layer) were commonly seen in the negatives in condition grades 3 to 5, reinforcing the regeneration of the anti-halation dyes along with increasing of degradation. Regarding yellowing, this hue was visually detected in case studies with assorted formats, however with incidence on case studies with notch code with 'square' shape.
In sum, SP collection provided a large amount of case studies with similar characteristics (brands, formats, and condition), allowing to perform a first identification of types of films that might be hazardous for film collections.
Aiming at crossing the macro assessment results accomplished for SP collection with another collection from the same period and with assorted brands, formats and film types, the Silva Nogueira was selected.

6.2.5 - Macro assessment of the case studies from Silva Nogueira collection

For this study, the results of the survey provided by the conservators working in ADF archive were considered. During the survey, an identification and assessment of the plastic negatives were carried out by the conservators, based on date information and visual assessment of the collection. In total, 9585 plastic negatives were surveyed.
From the specimens available for observation, twenty-two case studies were selected from this collection, two with 9x12 cm format and twenty with 13x18 cm format. The criteria for negative's selection are identical to those presented for other collections under study.
Despite the reduced number of case studies, this collection was selected with aiming at including examples of sheet film that could be compared with those found in the other collections and perform a comparative study focusing the behaviour of sheet films from different production contexts. Moreover, it was also aimed to know if there were different brands that could represent those indicated by the participants of the questionnaire presented previously[105] (e.g. Agfa-Gevaert and Perutz).

[105] See the results of the questionnaire in Chapter 4, pages 106 – 119.

Beside Kodak (or Eastman Kodak), no other brands were identified. As for San Payo's negatives, notch codes with 'U', 'V', 'square' and 'wide divot' shapes (alone or combined) were observed. Considering the small set of case studies selected, the eleven assorted notch codes found within this collection represents a remarkable variety of these marks. The list of notch codes surveyed along with the accurate identification of the film supports as accomplished by FTIR spectroscopy analysis is presented at the end of this chapter.

The condition of the specimens was also a selection criterium. Figure 6.19 depicts two case studies from Silva Nogueira collection illustrating conditions 1 (Fig. 6.19a) and 4 (Fig. 6.19b).

Figure 6.19 – Two case studies from Silva Nogueira collection (SN 1128 and 809) illustrating condition 1 (a) and 4 (b). Dates: 1954 (a) and 1950 (b). © DGPC-ADF/ Credit: Luisa Oliveira.

Occasionally, date information was observed on the edge of the image layer. The two case studies shown in Fig. 6.19 represent the method commonly used by Silva Nogueira to classify his work.

Comparatively with case studies from San Payo collection, in Silva Nogueira collection acetic acid odour was less noticed. In Figure 6.20, the several degradation signs detected in the case studies from Silva Nogueira are presented.

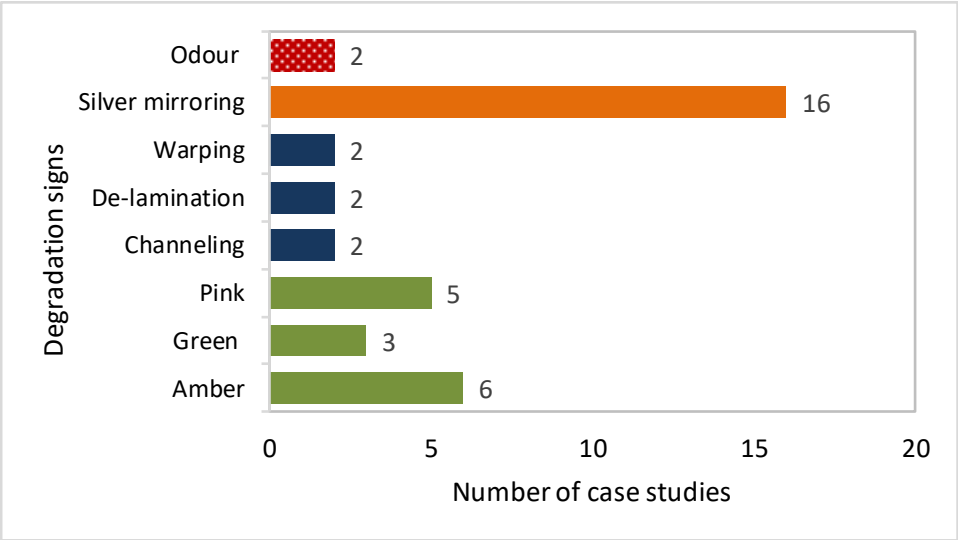


Figure 6.20 - Degradation signs visually assessed on the case studies selected from SN collection: acetic acid odour (red bar), silver mirroring (orange bar), change in shape and cohesion (blue bar), discoloration (yellow bars).

According to the macro assessment carried out, the two case studies with 9x12 cm format are in conditions 2 and 3. In Fig. 6.21, the condition of the case studies with 13x18 cm format are presented.

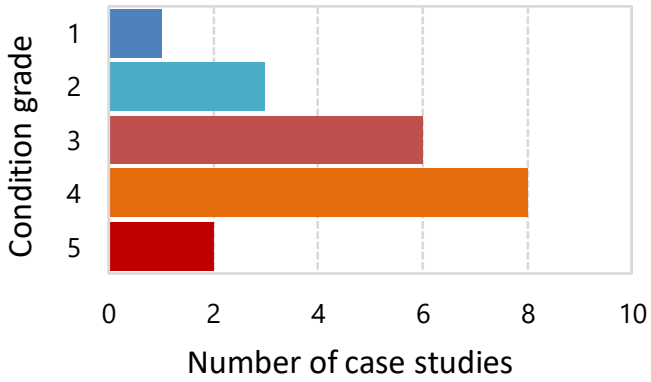


Figure 6.21 – Condition grades of the case studies with format 13x18 cm from the Silva Nogueira collection.

Based on the macro amassment results, most of the case studies from SN collection are in conditions 3 and 4 (Fair and Poor).

6.2.6 Compilation of the macro assessment results

From the five collections surveyed, 361 case studies were selected to macro assessed and sampled. They contained bot CN and CA supports. The formats ranged from small format (35mm), to medium format (60 mm) and large formats (9x12m, 10x15, 13x18 and 18x24 cm^2). Two different typologies of films were found in the set of films with 9x12 cm^2 format: 'Film pack' (present in DGEMN collection) and professional sheet film. Moreover,

the remainning sheet films are all portrait or professional type[106]. The case studies selected allow to verify the broad types of films and brands present within Portuguese collections and correlate these with the photographers choices regarding their professional work. The representativeness of the brands found were compared with those indicated in the questionnaire carried out in this work. Among the negatives which producer could be found it was concluded that Kodak is the most common brand in the photographic collections, maybe due its availability in the market or preference of photographers. Negatives from Agfa, Ferrania, and Ilford brands were also found. However, a large amount of the negatives had to be classified as Unknown since no brand could be identified. This result diverges from the results obtained with the questionnaire in which a residual percentage of participants (8%) replied having plastic negatives without brands references. Again, by comparing the results accomplished with the macro assessment with the questionnaire, Gevart, Agfa-Gevaert, Perutz and Fuji brands were not found.

Regarding dating, overall, besides ECC collection for which a definitive date of production is attributed, few date references were found per negative. Nevertheless, the period of production for each photographers or collections is known allowing to establish a time range in this work (Sena 1998; Mesquita and Pessoa 1995; Baptista 2015; Tavares 2011).

A broad variety of notch codes was surveyed, ranging from 'V', 'U', 'square' and 'wide divot' shapes, alone or combined. Beside the straightforward correlation between notch code and brand disclosed in the specimen, inconclusive results were obtained when attempting to correlate notch codes for specimens without brand identification embossed on the edge of the film. Aiming at contributing for a straightforward correlation between notch codes and film type, a list of the several notch codes found in the collections along with the accurate identification carried out by FTIR spectroscopy analysis will be presented.

Regarding the condition of the case studies, based on the macro assessment results, the negatives with large format tend to be more degraded that those with small and medium formats. However, it is important to mention that, except for ECC collection in which all negatives are in medium format, the amount of case studies with sheet films selected for this study superseded the amount of negatives with small and medium format. Additionally, a set of negatives with severe degradation was detected and correlated with notch code with a 'U' shape and blue anti-halation dyes. Beside blue hue, pink and green hues resulting from regeneration of anti-halation dyes were found in case studies from DGEMN, SP and SN collections. Moreover, pink, intense yellow, bluish, greenish, red-brownish and orange hues were visually perceived on the image layer of case studies from ECC collection, being suggested that it might result from different chemical solutions used to correct the density of the image. Additionally, in DGEMN, SP and SN collections, red and green ink masks were observed. According to the results, these two image treatments were used according to the intensions and aesthetic of the

[106] In Chapter 2, a summary of the technical characteristics of plastic negatives was presented.

photographers. For instance, the extensive presence of the aforementioned hues in case studies from ECC collection led suggesting that the photographer had technical problems with light and therefore he used chemical treatments to correct the density of the images. Moreover, except for specimens from MN collection, red and green masks were found in all collections.

The extensive observation and macro assessment carried out point out some of the issues that might be found in film collections held by Portuguese institutions. Yet, despite of the resemblaces with the reported in international researches, an accurate identification and assessment of those films that may later support decision making are still lacking. In the following section the identification and assessment of the case studies accomplished through analytical techniques will be presented.

6.3. Molecular assessment of the case studies under study

The supports of the 361 negatives selected were identified by FTIR spectroscopy. The identification of the film supports was based on the presence of the characteristic stretching vibrations associated to nitrate (CN) or acetate (AC) groups, respectively with characteristic features peaks for CN at 1655 cm^{-1}; 1282 cm^{-1}; 841 cm^{-1} (νONO_2) and peaks for CA at 1750 cm^{-1} (Ac $\nu C=O$) and 1234 cm^{-1} (Ac $\nu C-O$). Figure 6.22 depicts reference spectra, and corresponding peak assignment, for cellulose nitrate (left) and cellulose acetate, without additives (right).

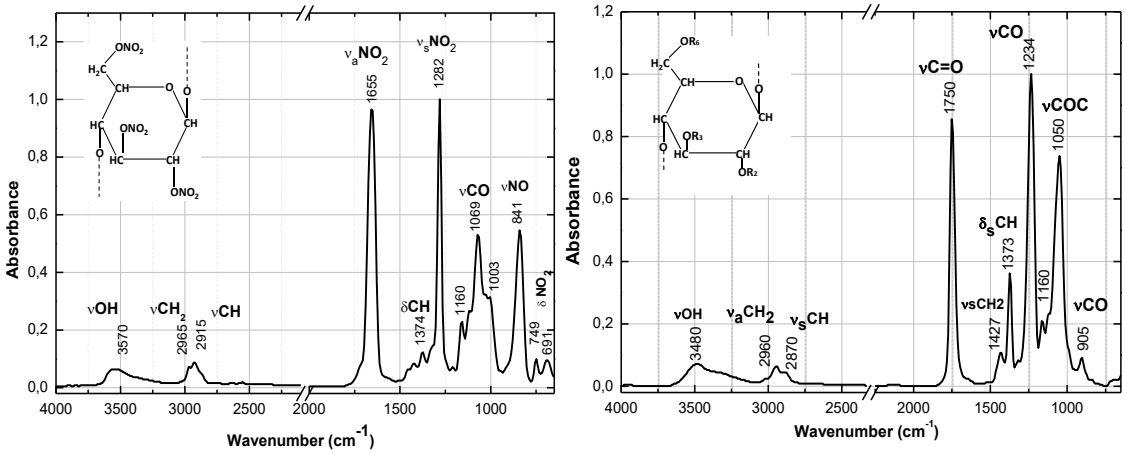


Figure 6.22 – FTIR spectra spectrum of reference cellulose nitrate (left) and cellulose acetate (right) films, without additives.

Beside the typical feature peaks for CN and CA, the characteristic peaks associated with the cellulose polymer in the 3500 – 3300 cm^{-1} region (O-H stretching), 2960 – 2870 cm^{-1} (C-H stretching) and strong absorbances in the region 1200 – 959 cm^{-1} (ring and pyranose C-O-C stretching) were identified (Zhbankov 1966). Comparatively with the FTIR regions indicated for cellulose polymer, minor shifts of the peaks caused by inter-

and intramolecular molecular forces resulting from esterification of cellulose may be found. Therefore, to improve the discussion about the identification of film supports, peaks assignment for CN and CA polymer are summarized in Table XII.1 (see Appendix IV). Moreover, besides identification, the intensity and shifts of peaks found in the FTIR spectra obtained from the analysis of the case studies allowed to assess the condition of these historical films.

Based on by μ-FTIR analysis the results it was possible to identify four types of cellulose derivatives, namely CN, CA, CTA and CAB.
Aiming at assessing the chemical and physical decay of these historical plastic negatives, pH and hardness (shore A) measurements were carried out. The results are presented for sets of case studies organized according to format or type of film support. Given the role of plasticizers in the stability (or decay) of film-based negatives, the identification of additives was carried out by μ-FTIR analysis and complemented with μ-Raman analysis. Identification and characterization of the film-based negatives selected for this study were also assessed by NIR spectroscopy. Given the unique character of the image hues found in the image layer of case studies from ECC and SP collections, μ-EDXRF and SEM-EDS analysis were performed and presented in the sections corresponding to each collection.

6.3.1. Molecular assessment of case studies from Elmano Cunha e Costa collection

According to μ-FTIR analysis it was possible to confirm that all 99 case studies from ECC collection are cellulose nitrate-based negatives. Alongside the characteristic absorption peaks associated to cellulose nitrate, in 98 case studies an additional peak in the carbonyl region (1740 cm^{-1}) was identified. According to the literature, the peaks found at 1733 cm^{-1}, as well as at 2963 cm^{-1} and 2874 cm^{-1} are associated with camphor (Stewart 1997, 86; Quye et al. 2011, 1372). Moreover, four case studies exhibit peaks at 1457, 1488, 1187 and 960 cm^{-1}, which are attributed to plasticizers such as triphenyl phosphate (TPP) and phthalates (Schilling et al. 2010). The use of these additives to improve the properties of CN polymer is known[107]. The results accomplished with FTIR spectroscopy analysis allowed to distinct three types of formulations in which aforementioned plasticizers were used alone or combined: i) only with camphor (95 case studies), ii) camphor combined with phosphates and phthalates (3 case studies[108]), and, iii) phosphates and phthalates (1 case study[109]). This finding agrees with the literature (Glafkidès 1949; Saunders and Taylor 1990; Shashoua 2008). However, acknowledging the reference to the purchase of Agfa films found in invoices of material acquired by Cunha e Costa, it was questioned if once this information is valid and indicates that Cunha e Costa selected this brand to

[107] See Chapter 2, pages 37-39.
[108] Case studies with indexation number (nº) ECC 1256, 4466, 8518.
[109] Case study with indexation nº ECC 8702.

perform his work. If so, this would mean that in the 1930's Agfa used different formulations to plasticize cellulose nitrate-based negatives. On the other hand, it may also be considered that Cunha e Costa bought cellulose nitrate-based negatives from different brands. The lack of brand identification on the edge of the films inhibit such conclusion. Therefore, it can only be suggested that, in the 1930's at least three types of plasticizer formulations (alone or combined) were being used to improve the properties of cellulose nitrate-based negatives.

Figure 6.23 depicts the FTIR spectra for camphor (a), triphenyl phosphate (b), diisobutyl phthalate (c), dibutyl phthalate (d) and case study ECC 4466. It is apparent the presence of camphor combined with other plasticizers in this case study.

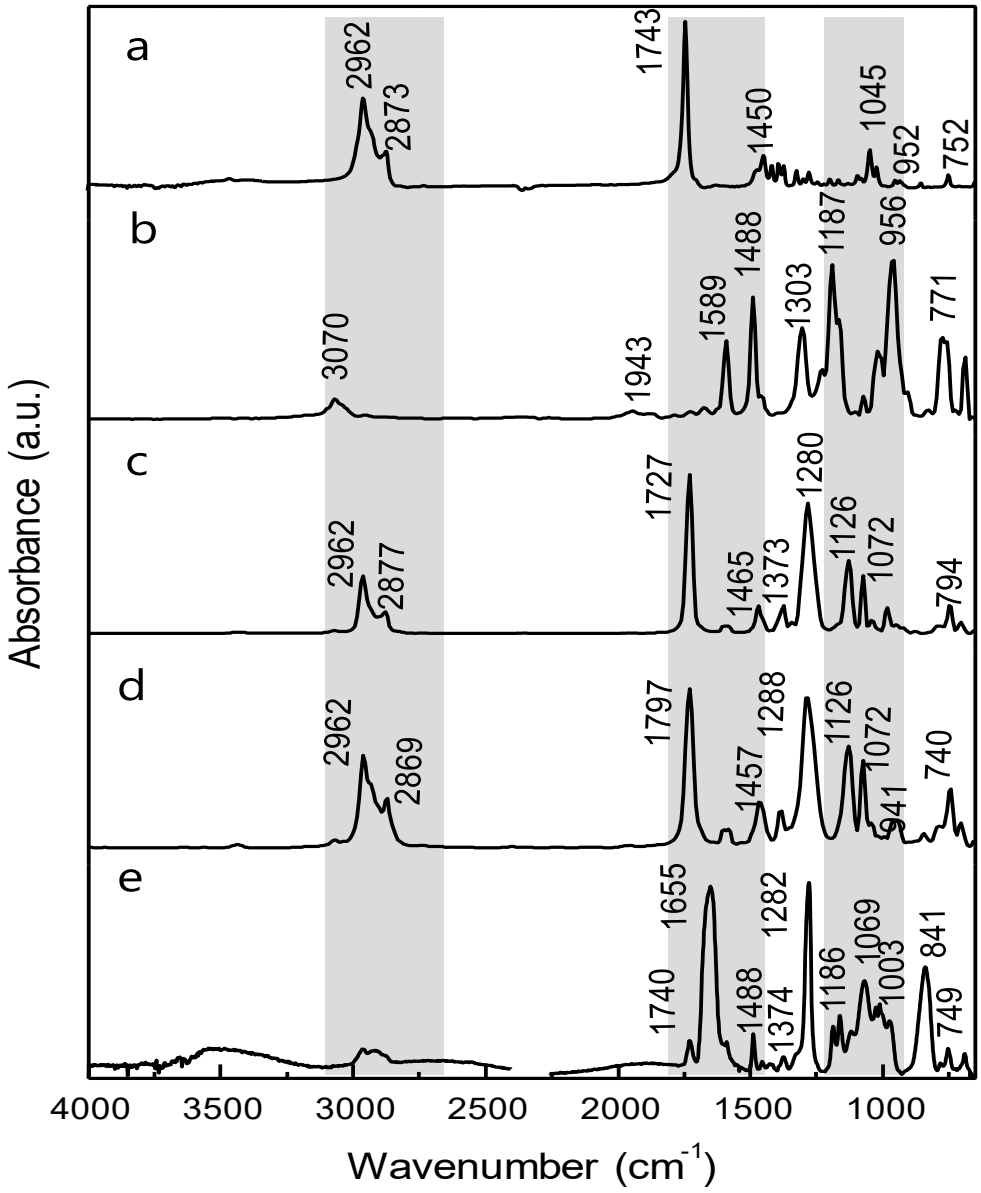


Figure 6.23 – FTIR spectra of camphor (a), triphenyl phosphate (b), diisobutyl phthalate (c), dibutyl phthalate (d) and case study ECC 4466 (e) (exhibiting the peaks associated with camphor at 1740 cm^{-1}, and peaks attributed to TPP and phthalates at 1488, 1489, 1187 and 960 cm^{-1}, grey regions).

Beside the accurate identification of the film's composition, FTIR spectroscopy was also used to assess the condition of the film support. The selection of the peaks for this study relied on the information that could be taken from each region of the spectra. For instance, the spectral changes in the O-H stretch region at 3570 cm^{-1} are pointed out as a marker for degradation. However, these changes may be correlated with unsubstituted hydroxyl groups of cellulose that have not reacted during the esterification process or with the hydrolytic decay of CN (Quye et al. 2011). Moreover, the CN-camphor complex may be based on the bonding *between the carbonyl group of the camphor molecule* with the non-substituted hydroxyl group present in the cellulose dinitrate (Yarsley and Flavel et. al, 1964, as cited in Sirkis 1982, 8). For these reasons, it was considered that the O-H stretch region would not allow to reach conclusive results regarding the assessment of the case studies.

The peak ratios discussed in former studies were reviewed. In previous investigations, the peak ratios $\nu_s C{=}O$ 1733 cm-1 / $\nu_a NO_2$ 1660cm-1 and $\nu_s NO_2$ 1294 cm-1/ $\nu O\text{-}NO_2$ 875 cm-1 (Edge et al. 1990); and $\nu_s C{=}O$ 1733 cm-1 / $\nu C\text{-}O\text{-}C$ 1070 cm-1 (Saunders as citted in Quye et al. 2011) were proposed to monitor CN decay. Moreover, the peak ratio $\nu_a NO_2$ 1650 cm-1/ $\nu_s C{=}O$ 1733 cm-1 was used for monitoring the formation of degradation products resulting from CN's decay (Edge et al. 1990; Y Shashoua et al. 1992). According to the authors, the carbonyl region (C=O) allows to assess CN's decay, however, as previously said, the carbonyl region is also associated with the presence of camphor and other plasticizers (Quye et al. 2011). Regarding that the carbonyl (ketone) group in camphor might be linked to the nitrate groups[110], in this study, the use of the peak at 1733 cm^{-1} was excluded since the analysis of the infrared spectra in the C=O region would be inconclusive or could lead to misinterpretations.

Moreover, the ether absorption at 1070 cm^{-1} was highlighted for being unaltered in the initial stages of degradation (Jutier et al. 1987). Nevertheless, in the course of degradation, these bonds will break due to hydrolytic degradation (Quye et al. 2011), as seen in an investigation on cinematographic films in which major changes of the peaks at 1118, 1160 and 1206 cm^{-1} (C-O-C stretching region) were observed. These changes seen in the C-O-C stretching region indicate chain-scission of the backbone of CN polymer, disclosing the decrease of the physical properties of the materials/objects (Edge et al. 1990).

Considering the facts presented, to estimate the extent of degradation of the case studies from ECC collection, the peaks at 1650, 1282 and 841cm^{-1} associated with nitrate group were rationed against the peak at 1374 cm^{-1} (C-H bending vibration). Although poor absorption was consistently observed for the peak at 1374 cm^{-1}, this peak was selected because it remained relatively unchanged for the case studies from ECC collection.

[110] See Chapter 2, page 38, where the CN-camphor system is discussed.

On the other hand, given the different degradation kinetics[111] between the C-O-C stretching region and NO_2 stretching regions, the peak ratios $\nu_a NO_2$ $_{1655\ cm^{-1}}$ / νCOC $_{1160\ cm^{-1}}$ and $\nu_s NO_2$ $_{1282\ cm^{-1}}$ / νCOC $_{1160\ cm^{-1}}$ were calculated. In this way, it was possible to follow the decrease of the intensity of the peaks associated with -O-NO_2 stretching vibrations at 1655 and 1282cm^{-1} that reflect the cleavage of the nitrate group (denitration) and consequent formation of •NO_2, and assess changes in the C-O-C stretching region (Edge et al. 1990; Quye et al. 2011; Berthumeyrie et al. 2014; Bussiere, Gardette and Therias 2014).

The FTIR spectra of five case studies from the ECC collection and an unaged film are presented in Fig. 6.24, showing changes mostly in the O-NO_2 stretching absorptions at 1655, 1282 and 841 cm^{-1}. Minor changes are seen in the O-H stretch region at 3570 cm^{-1} and C-H stretching absorptions at 2960 and 2915 cm^{-1}. It is also observed a decrease on the intensity of the peak at 1069 cm^{-1} which is probably associated with the decrease of the nitrate groups (Zhbankov 1966).

To illustrate the results obtained by FTIR spectroscopy analysis, it was chosen to select the spectra with good resolution from five case studies (with camphor), that would allow to compare the results and understand the molecular differences between them. Moreover, these spectra are also representative of the peak ratios determined.

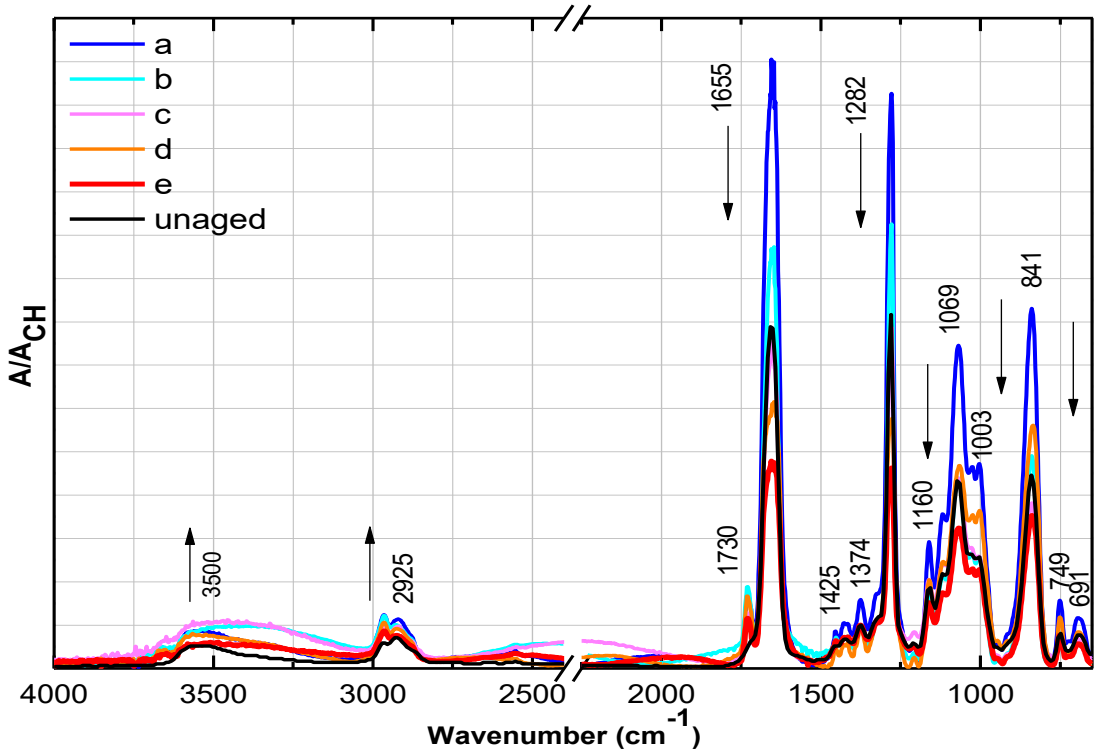


Figure 6.24 – Infrared spectra of five case studies from ECC collection and a cellulose nitrate unaged film (black), with absorptions normalized for CH bending (1374 cm^{-1}). Case studies: ECC 981 (a), ECC 554 (b), ECC 2763 (c), ECC 2930 (d) and ECC 2804 (e).

[111] According to Jutier (1987) this behaviour is a consequence of the lower dissociation energy required to break O-NO_2 bonds, comparatively with C-C and C-O bonds.

The spectra obtained in this study show minor increase of the intensity in the O-H stretching region, with intensities ranging from 0.13 to ~1.8. This range of intensities in the O-H stretching region is not exclusive and therefore does not allow to differentiate and evaluate the degradation condition of the case studies from ECC collection. On the other hand, it may be pointing out for the Good condition of this set of negatives. Moreover, a shift of the peak at 3570 cm $^{-1}$ to lower wavenumbers and an insignificant broadening of the peak detected in a small set of samples (34) were observed. In the same way, minor increases on the intensity of the C-H stretching absorptions at 2960 and 2915 cm^{-1} is observed. Given the results obtained in the O-H (3570 cm^{-1}) and C-H (2960 and 2915 cm^{-1}) stretching regions, it was decided that, for this study these two regions are ineligible for the evaluation of the conservation condition of the case studies from ECC collection. As it is shown in Fig. 6.25, by organizing the peak ratios from the highest to the lowest values obtained, an agreement on the decrease of the intensities of the peak ratios $\nu_a NO_2$ $_{1655\ cm^{-1}}$ / $\delta CH_{1374\ cm^{-1}}$ and $\nu_a NO_2$ $_{1655\ cm^{-1}}$ / νCOC $_{1160\ cm^{-1}}$ was found.

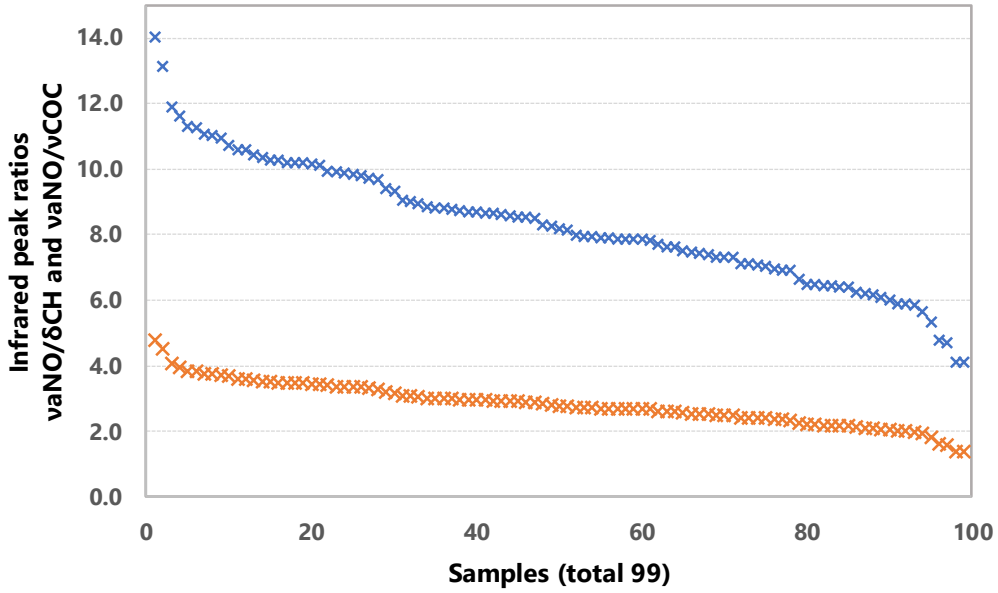


Figure 6.25 – Infrared peak ratios $\nu_a NO_2$ $_{1655\ cm^{-1}}$ / $\delta CH_{1374\ cm^{-1}}$ (blue cross), and $\nu_a NO_2$ $_{1655\ cm^{-1}}$ / $\nu COC_{1160\ cm^{-1}}$ (yellow cross) (absorptions intensities) of the case studies from ECC collection.

Thus, according to the results obtained the peak ratios $\nu_a NO_2$ / δCH and $\nu_a NO_2$/ νCOC showed to be suitable for the condition's assessment of the film support of the case studies from ECC collection. Given the large set of case studies selected from ECC collection it was decided to disclosure the peak ratios accomplished as in Fig. 6.25[112].

[112] In Appendix V, Table V.1, the intensities for peak ratios $\nu_a NO_2$ / δCH; sνNO_2/ δCH, νO-NO_2 / δCH and $\nu_a NO_2$/ νCOC peak ratios (absorptions intensities) per each case study from the ECC collection are presented. Additionally, visual assessment classification, and average measurements and standard deviation (SD) obtained from pH and hardness (Shore A) measurements are given.

According to the results presented in Fig. 6.25, by determining the peak ratio $\nu_a NO_2$ / δCH, the loss of nitrate groups could be assessed. In this way, it is possible to suggest that in most of the case studies denitration (loss of nitrate groups) is occurring. Since in this set of case studies lacks an example of severe degradation, the data obtained do not allow to establish a degradation marker. However, it allows to reach a range of intensities with which it may be possible to compare the results accomplished by analysing the case studies from the other collections scoped. Moreover, regarding the peak ratio $\nu_a NO_2$/ νCOC, a minor decrease was observed, allowing to suggest that minor changes are occurring in the backbone of the polymer. The data obtained is in agreement with the literature in which it is proposed that, at a first stage, the polymer denitrates (homolytic scission of $CO\text{-}NO_2$) and later, degradation products will lead to an exponential degradation process (autocatalytic point) that will result in the scission of the cellulose chain (Edge et al. 1990, 623; Stewart 1997, 18).

Additionally, minor shift of the peaks in the $O\text{-}NO_2$ stretching absorptions at 1655, 1282 and 841 cm^{-1}, and C-O-C stretching region at 1060 cm^{-1} were seen. In Fig. 6.25, peak shifts for the aforementioned regions found for five case studies from ECC collection with different visual assessment grade (ECC 981 – grade 1, 554 – grade 4, 2763 – grade 2, 2930 – grade 3 and 2804 – grade 2) which are representative of the peak ratios 14.0, 9.7, 7.5, 6.1 and 4.8, respectively, are presented. The selection of these case studies for representing the FTIR peaks shifts of the set of case studies from ECC collection relied on the intensity of the peak's ratios and spectral resolution of the spectra.

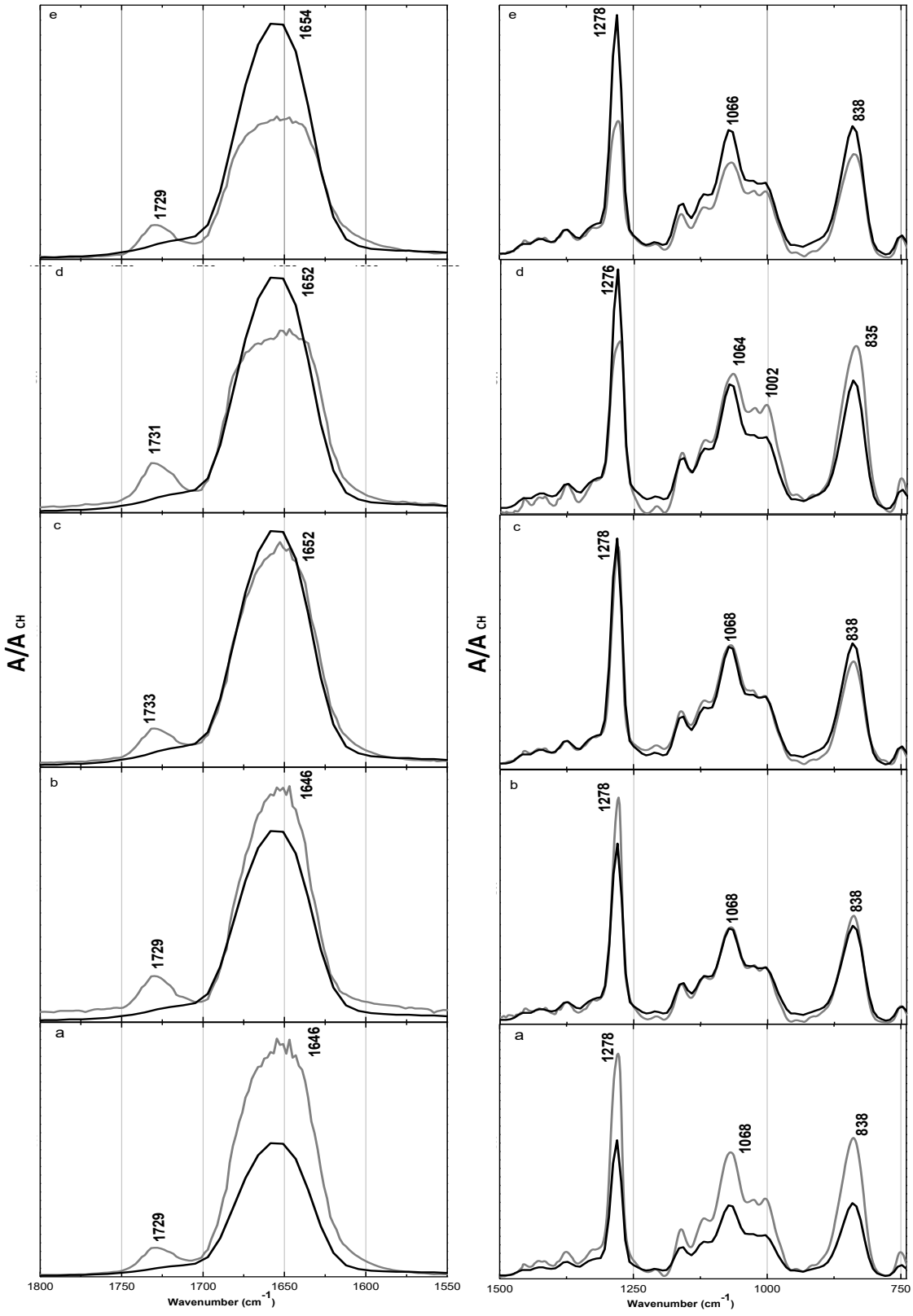


Figure 6.26 – Infrared spectra of unaged film (black) and five case studies from ECC collection (grey) showing different condition grades: C=O stretching region (left), and O-NO_2 stretching, C-H bending and C-O-C stretching regions (right). Spectra with absorptions normalized for CH bending (1374 cm^{-1}). Case studies: ECC 981 (a), ECC 554 (b), ECC 2763 (c), ECC 2930 (d) and ECC 2804 (e).

As shown in Fig. 6.26, no relevant peaks shift was found. Nevertheless, in order to evaluate possible denitration, a closer observation of the O-NO_2 stretching (1655,1280 and 840 cm^{-1}), and carbonyl peak attributed to camphor (1733 cm^{-1}) was performed by fitting with a Gaussian function. Moreover, the infrared absorptions at C-O-C stretching region (1060 cm^{-1}), normalized for δCH at ~1374 cm^{-1} were evaluated. In Table 6.2 The results obtained are presented.

Table 6.2 – Case studies from ECC collection: fitting parameters for NO stretching ($_{1655,\ 1282\ and\ 841\ cm^{-1}}$), correlation coefficient (ρ), peak centre (μ), peak height (H) and full width at half height (σ); COC stretching ($_{1060\ cm^{-1}}$) peak height (H), peak normalized for δC-H at ~1374 cm^{-1}.

Sample	ν_aNO_2 1655 cm^{-1}				ν_sNO_2 1282 cm^{-1}				νNO_2 841 cm^{-1}				νCOC 1060 cm^{-1}	
ECC	ρ	μ	H	σ	ρ	μ	H	σ	ρ	μ	H	σ	μ	H
981	0,99	1654,9	14,2	51	0,98	1281,9	12,7	23,6	0,98	842,5	7,7	47,8	1068	7,45
554	0,99	1655,2	9,5	45,1	0,98	1281,4	9,4	21,1	0,98	842,6	4,6	44,8	1068,4	4,38
2763	0,99	1655,0	7,4	51,3	0,98	1281,4	6,9	21,5	0,99	841,5	3,5	47,9	1068,4	4,38
2930	0,97	1654,9	6,4	59,2	0,96	1281,9	5,4	28,6	0,97	840,8	5,4	51,4	1064,5	4,67
2804	0,98	1654,7	4,8	57,3	0,97	1282,0	4,1	26,3	0,98	841,6	3,4	51,4	1066,5	3,24

According to data presented in Table 6.2, it is possible to confirm that there is no relevant peak broadening or shift. However, changes on peak height (H) were found, indicating the decrease of nitrate groups per each negative. Thus, by comparing the peak ratios, Gauss fitting and peaks' shift, it is possible to suggest that side-chain reactions are taking place at least for the films with peak ratios bellow 12 and 4 resulting from the ν_aNO_2 / δCH and ν_aNO_2 / νCOC ratio determination, respectively.

pH

The decrease of pH is known as an indicator of the chemical decay of cellulose derivatives (Edge et al. 1990; Adelstein et al. 1992; Adelstein et al. 1995a; Adelstein et al. 1995b; Bussiere, et al. 2014). To support the results obtained by FTIR spectroscopy analysis, pH measurements were carried out aiming at finding a correlation between the decrease of nitrate groups and consequent decrease of pH. The potentiometric method selected, in which micro-electrodes were used, allowed to assess four independent areas of the case studies. As described, the pH measurements were performed on the back (anti-curling layer) of the negatives.

The average pH measurements obtained range between ~3 and ~6. For one exceptional case study, ECC 1256, it was not possible to measure pH because after applying the water on the surface of the negatives, the water was completely absorbed. Two hypotheses were considered for this phenomenon, one is the decay of the gelatine caused by degradation products resulting from the cellulose nitrated-base. However, the peak ratios (IR absorption intensities) obtained for this case study are one of the highest

determined for the set of studied films from ECC collection. On the other hand, it is suggested that this phenomenon may be related with the fact of the gelatine layer within the ECC 1256 negative being, for unknown reasons, different from the others. As it is known, the diversity of the gelatine compositions could vary according to photographic materials (negatives, prints, etc.) but also according to manufacturer (Hendriks et al. 1984).

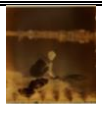
Thus, based on the results obtained for the all set of negatives, no correlations were found between the decrease of the absorption intensities at the FTIR regions associated with NO stretching or even with C-O stretching (ring and pyranose C-O-C stretching). In part, this result may be related with the fact of the pH measurements being carried out on the surface of the gelatine layer. As previously described in this work[113], photographic gelatine was hardened to increase its viscosity and melting point, decrease the swelling ability and improve the resistance to mechanical stress (Mees 1942b, 100). Thus, the pH measurements may reflect the hardening compounds present at the surface. Or, the pH values obtained may result from possible contaminations or deposits impregnated on the gelatine layer. Other causes may arise from gelatine´s scavenging behaviour was acknowledged (Edge et al. 1990), and the detrimental effects that degradation products (e.g. NO_x) may have a catastrophic effect on the gelatine layer (Carrol and Calhoun 1955; Nguyen et al. 1997).
Thus, taking into consideration the overall FTIR data and pH results obtained on films from ECC collection, it is possible to suggest that at a molecular level these are still in a good condition. Or, on the other hand, gelatine may be scavenging the initial degradation products formed.
Nevertheless, a closer observation of the differences in the pH values revealed that the results may be related with specific areas of the specimens. Initially it was thought that these results could be in accordance with heterogeneous degradation within the same specimen. Since FTIR results may represent the chemical behaviour of an area rather than the overall specimen, this relationship could not be performed in this study. A careful observation of the case studies allowed to associate the pH values with image density, stains, discoloration and/or degradation. As an example, negative ECC 5143 shows different hues (amber at the top and no hues of the bottom) (Fig. 6.27). The top area of the negative (amber) has an average pH value of 5 while bottom (no discoloration) have pH 4. These minor differences are reflected in the SD of the pH measurements.

[113] See section 3.2.1, page 53.

Figure 6.27 – Case study ECC 5143, from ECC collection with different hues and different pH values. Top: ambar hue, pH c. 5. Bottom: no hue, pH c. 4.

This possible relationship expanded the interest on identify the origin of the hues found on the image layer of the negatives and its possible effect on pH.
From the total set of case studies, fourteen were selected. Beside three negatives lacking hues (selected as standards), the remaining negatives selected show tonalities ranging from intense yellow (2 negatives), pale pink (3 negatives), red-brownish (2 negatives), orange-brownish (3 negatives) to pale green (1 negative). The samples were organized into six groups (from A to F, named grA etc.) according to the tonality presented. In Table 6.3 the results obtained by micro- EDXRF and SEM-EDS are presented as well as pH, hardness, colorimetry and infrared spectroscopy results.

Table 6.3 - Results from colourimetry, molecular analysis µ-EDXRF **(major** and (minor) chemical elements), µ-FTIR analysis (peak ratios $\nu_s NO_{2\ 1655cm-1}$/ δCH_{1374cm}^{-1}), pH and proposal of chemical treatments performed on b/w film-based negatives of ECC collection.

(gr)	Ref.		*L** *a** *b**	µ-EDXRF	µ-FTIR	pH	CONCLUSION
A	ECC 1256		31±2 0.4±0 1±0.5	Ca, Cr, Ag, Fe, Zn, S, Cl	13.6	-	No chemical elements linked to corrective treatments
	ECC 2413		30±0.7 0.4±0.1 0.9±0.2	Ca, Fe, Ag, S, Cl	6.4	4±0.4	No chemical elements linked to corrective treatments
	ECC 2518		33±0.2 0.5±0 2±0.1	Ca, Cr, Fe, Ag, S, Cl	6.9	5.4±0.2	No chemical elements linked to corrective treatments
B	ECC 981		74±0.8 10±0.5 15±0.5	**Hg**, **Cr**, (Ca, Ag, Cl)	14	5.3±0.1	*Subtractive reduction* Mercury and cyanide[(a)] (Eder's solution)
	ECC1616		61±3 9±0.2 15±0.7	**Hg**, **Cr**, (Ca, Cl, Ag)	10.2	4.3±0.4	*Subtractive reduction* Mercury and cyanide[(a)] (Eder's solution)
	ECC1228		59±0.6 7±0.6 14±0.7	**Hg**, **Cr**, **Fe**, (Ca, Cl, Ag)	6.5	5.5±0.1	*Subtractive reduction* Mercury and cyanide[(a)] (Eder's solution)
C	ECC 286		30±0.3 2±0.3 3±0.5	**Cr**, (Ag, Fe, Zn, S, Cl)	10.4	3.6±0.1	_____
	ECC 631		28±0 0.5±0 0±0	**Cr**, (Ag, Fe, Zn, S, Cl)	11.3	3.7±0.2	
D	ECC2641		44±2 1±0.3 10±1	**Cr, Hg**, **I**, (Ca, Zn, Ag, Cl)	7.3	5.5±0.3	*Subproportional Intensification* Mercuric Iodide
	ECC 879		63±2 13±0.5 47±2	**Cr, Hg**, **I**, (Ca, Zn, Ag, Cl)	10.6	5.8±0.1	*Subproportional Intensification* Mercuric Iodide
	ECC2799		81±2 1±1 46±3	**Hg**, **I**, (Ca, Zn, Ag, Cl)	8.8	5.4±0.1	*Subproportional Intensification* Mercuric Iodide
E	ECC2203		29±0 1±0 1±0	**Fe,** (Ca, Cr, Ag, Zn Cl)	4.1	4.2±0.3	_____
	ECC 2282		30±0 1±0 2±0	**Fe,** (Ca, Cr, Ag, Zn Hg, Cl)	7.9	4.5±0.3	
F	ECC5142		31±0 3±0 4±0	Cr, Ag, Fe, Zn, S, Cl	10	3.4±0.1	_____

µ-EDXRF results

The µ-EDXRF analysis was performed firstly for identification of the chemical elements in the image and secondly to correlate those results with the hues visually perceived and establish possible correlations with pH measurements obtained. The indication of the elements as major and minor was made based on the relative intensity of the peak's characteristic of each element, being established that the major elements (proposed in Table 6.3) present at least twice the intensity comparing with the correspondent peaks' intensities obtained for the remaining negatives. Figure 6.28 depicts µ-EDXRF spectra obtained for per sample and groups indicated in Table 6.3.

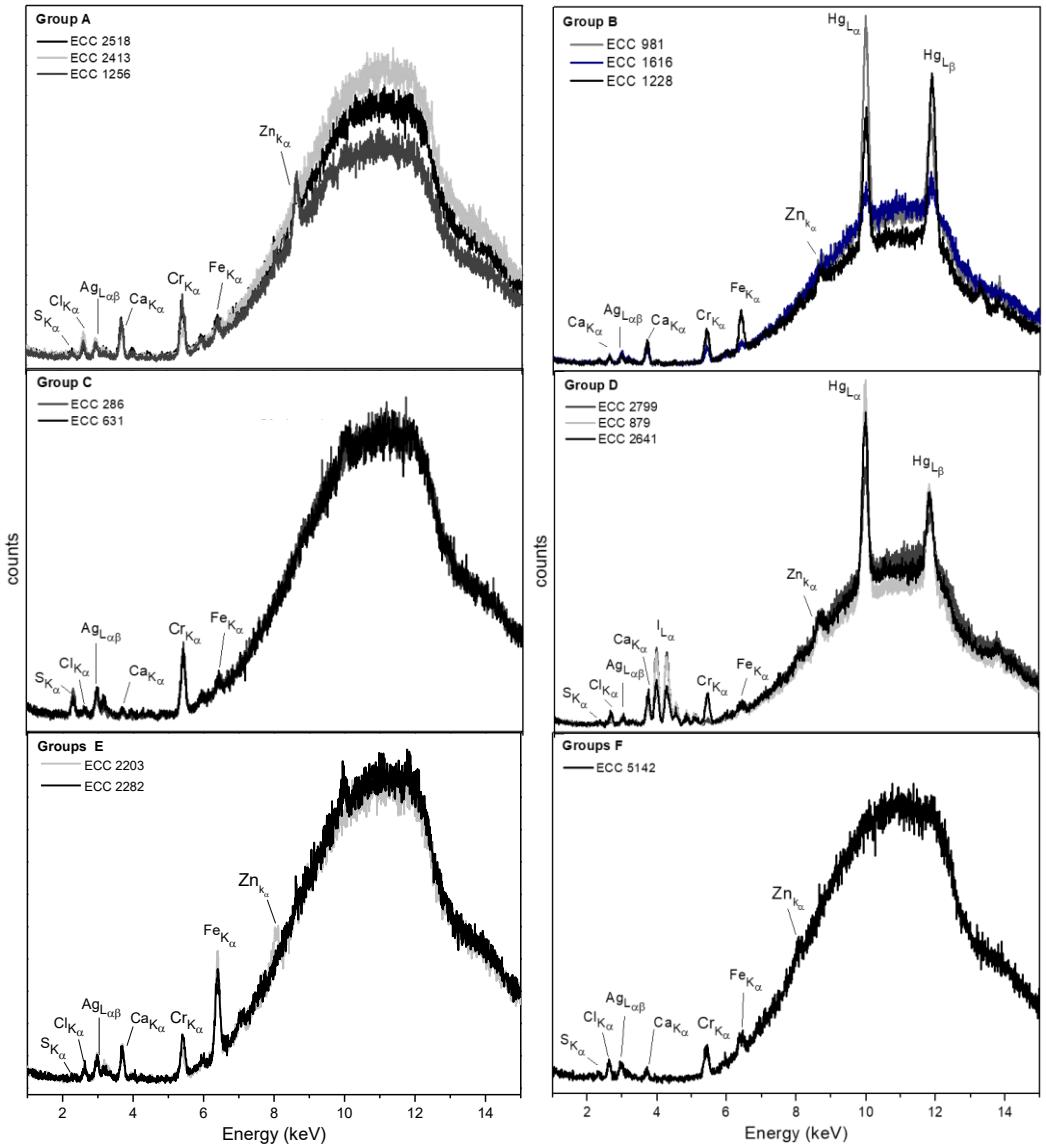


Figure 6.28 - µ_EDXRF spectra obtained from the analysis of the image of the all the negatives from Group A to F.

The presence of calcium, chromium, silver, iron, zinc, sulphur, and chlorine was identified in all negatives (Fig 6.28). Additionally, mercury and Hg and iodine were identified in grB and grD, respectively (Fig 6.28). Data obtained point out for a possible correlation

between pink hue and mercury (grB Eder's corrective treatment). The yellow and greenish hues are correlated with mercury iodide solution (grD) (Lavédrine and Garnier 1989).

Regarding the presence of Ca, the plastic negatives from ECC collection were stored on metal boxes filled with calcium carbonate to prevent the effects of moisture and high temperatures of Angola. The storage boxes no longer exist; therefore, it was not possible to analyse them. However, the consistency of the results allows proposing that the presence of Ca results from the storage system. The µ-EDXRF analysis also allowed to identify the presence of Zn. Two hypotheses were considered for the presence of Zn, one is the composition of the metal boxes used by Cunha e Costa (Castelo and Mateus 2014) and the other is the possible use of zinc hypochlorite solution (Flandreau's eliminator) for removing *the* fixing agent (sodium or ammonium thiosulphate) (Crabtree et al. 1940). The first hypothesis was also supported by the information disposed in a Portuguese photographic magazine from the beginning of the 20th century, in which the use of quoting: 'zinc boxes with reservoirs in the bottom filled with lime chloride' were recommended to prevent the detrimental effects of high relative humidity (Santo 1907) . Despite of the information gathered, in the framework of this study it was not reach any conclusions regarding the origin of Zn on the films since the storage boxes used by *Cunha e Costa* do not exist. Additionally, further work must be performed to assess the quantities of Zn left by treatments performed with the Flandreau's solution.

Regarding the presence of Cr, this may result also from *permanent* or *temporary hardening* of gelatine. Commonly, *temporary hardening* was performed by the photographers as a preventive action to avoid the gelatine swelling, peptization and physical damage in *'hot seasons or tropical climates'* (Mees 1942a). Nevertheless, Cr, as other inorganic and organic hardening agents, were commonly used for industrial production of gelatine emulsions (Mees 1942a). Fe is one of the possible inorganic hardeners commonly used. Thus, the presence of this chemical compound on the case studies from ECC collection may result from permanent hardening (Neblette 1952; Mees 1942a; Glafkidès 1987), or due to residues left from the water used during photographic processing. Although these two hypotheses may be suitable for most of the negatives of the set, the detection of peaks with twice the intensity for negatives from grE and the orange-brownish hue of those allows proposing that the negatives from grE have been treated with a corrective solution containing Fe.

Concerning colours visually perceived on negatives from groups C and F, it was not found a clear correlation between µ-EDXRF and colour. However, and according to literature, the colour can be a consequence of thiosulphate residues or due to *toning intensification* performed to increase the opacity and the contrast of the image through the formation of yellow to brown hues (Neblette 1952; Mees 1942a). These hues will act as "filters" absorbing blue light. Identical characteristics were visually perceived in negatives from groups C and F. The chemical compounds used in the main toning processes were sulfur, copper, uranium, vanadium and iron (Nebblet 1931).

In sum, all types of intensification methods promote the formation of colours. According to μ-EDXRF results and colour measurement results, it is possible to suggest a correlation between colour and chemical elements used to perform corrective treatments of the image (Table 6.3).

SEM-EDS results

To clarify the presence of the chemical elements identified by μ-EDXRF, SEM-EDS analysis of the cross-section of four negatives was carried out: ECC 2518, ECC1228, ECC 879, and ECC5142, each one representative of the groups A, B, D and E, respectively. The analysis of the support, photographic emulsion and anti-curling layers gave insightful information concerning the presence and origin of chemical elements identified by μ-EDXRF analysis. The predominant percentages found are attributed to carbon and oxygen (above 90 at. %, atomic percentage), which are associated with gelatine layers (photographic emulsion and anti-curling layer) and CN support. No chemical elements were detected on the support and anti-curling layer. Therefore, all elements were on photographic emulsion supporting the theory that except for negative ECC 2518 a corrective treatment of the image with different solutions was performed.

Vestigial percentages of Si (0.1 to 1.5 at. %), Cl (0.2 to 6.3 at. %) and Ca (0.03 to 0.9 at. %) were detected. The presence of Cl and Si was not clarified in this study, being demanded further work. The vestigial presence of Ca maybe related with storage or with photographic processing. By SEM-EDS analysis the presence of Al on negatives ECC 5142 (grA) and ECC 879 (grD) in percentages ranging from 0.5 to 1.6% (at. %) was identified. Additionally, Cr, Fe, Cu were also identified. Al^{3+}, Cr^{3+}, Cu^{3+} and Fe^{3+} were used as gelatine hardeners (Mees 1942b). Based on at. % obtained for Cr (10 to 21% at. %) and μ-EDXRF data is possible to propose that Cunha e Costa consistently used Cr as temporary hardening agent rather than as a corrective treatment. The low percentage of Fe (0.3 at. %) detected in negatives ECC 2518 and ECC 1228 allows suggest that its presence results from residues left on the image during processing. Unique assignments for Cu and Zn were identified for negative ECC 5142 (grF). Therefore, there is no clear justification for the presence of those elements. Furthermore, Ag, Hg and I (2.4%, 2.8% and 0.09% at.%, respectively) were identified for negative ECC 879 (grD).

Unlike μ-EDXRF results, Zn was only confirmed for negative ECC 5142 (grF), demanding further research to understand the presence of this chemical element. Apart from negative ECC 1228 (grB) for which it was not detected Hg as expected, the SEM-EDS results allowed to support the μ-EDXRF results. Additionally, SEM-EDS results confirmed that the chemical elements were present on the photographic emulsion, thus on the emulsion layer rather than on the film base or on the anti-curling layer.

SEM-EDS and μ-EDXRF results are relevant if considered that transition metals may induce the degradation of cellulose ester films (Edge et al. 1990; Edge et al. 1989; Shashoua 2008). Given that gelatine is permeable the risk of penetration of these

transition metals into the film base and its contribution for film decay must be considered.

By crossing µ_EDXRF and pH results, e.g. the data obtained for negatives from groups B to E, a possible correlation is suggested. Particularly for groups C and F for which µ-EDXRF analysis confirmed that Cr is the main element present in the image, lower pH values were recorded. Further work on a larger set of negatives must be performed to confirm this possibility.

Colourimetry

Although the colours on the negatives are visually perceivable, it seemed relevant to perform colour measurements to obtain quantitative data supporting the differentiation between warmer colours from groups C, E and F. The $L^*a^*b^*$ values presented in Table 6.3 are the result of 24 measurements for each negative.

Regarding the L^* coordinate, groups B and D have the highest L^* values obtained while groups A, C, E and F have the lowest. As expected, the highest a^* values were obtained for negatives grB (pink colour) while the lowest a^* values were recorded for negatives from groups C, E and F. Moreover, it was found that in opposition to the other negatives from grD, the negative ECC 879 has the highest a^* value due to its greenish tonality. Concerning the b^* coordinate, highest b^* values were obtained for negatives with yellow hue from grD, followed by negatives from grB probably due to general light yellowing which is visually perceivable. Lower values were obtained for negatives from the other groups (A, C, E and F). Overall, the standard deviation found for colour measurements show a low variation of the L^*, a^* and b^* values that result from heterogeneities on density and colour intensity of each negative. The data obtained do not support the differentiation of negatives from groups C, E and F (Table 6.3).

Hardness

With the aim to assess differences on the mechanical behaviour that would result from the chemical decay of the polymeric support hardness (Shore A) measurements were carried out. With this non-destructive method it was possible to perform four hardness measurements in four different areas of the object. Again, the measurements were carried out on the back of the negatives. The average hardness values obtained are very similar for most of the case studies from ECC collection with the exception of ECC 2005 for which the lowest average hardness value was obtained (97.4±1.4), and ECC 2799 and 7959 (98.2 ±0.9 and 98.4 ±0.4 shore A, respectively). The remaining 96 case studies have average hardness values of ~99 shore A. Regarding the assessment of the mechanical properties of the case studies from ECC collection, according to the data presented minor changes were found, which in part may be correlated with the µ-FTIR analysis results, that indicate that the minor spectral changes are occurring the film base. Thus, given the results obtained it is suggested that the set of case studies from ECC collection are all in

good condition, showing no deformation or brittleness (corresponding to macro assessment results).

VA and molecular assessment (MA) correlation

Regarding VA and MA results obtained, attempts to correlate both were made. The data collected (FTIR peak ratios, pH and hardness) per case study was organized according to the VA classification. From that point, the average and respective standard deviation of FTIR peak ratios, pH and hardness per VA condition grade was calculated for each set of films. In Fig. 6.29, the results obtained for peak ratios ν_aNO_2 / δCH, and ν_aNO_2/ νCOC, as well as the average pH values, are presented.

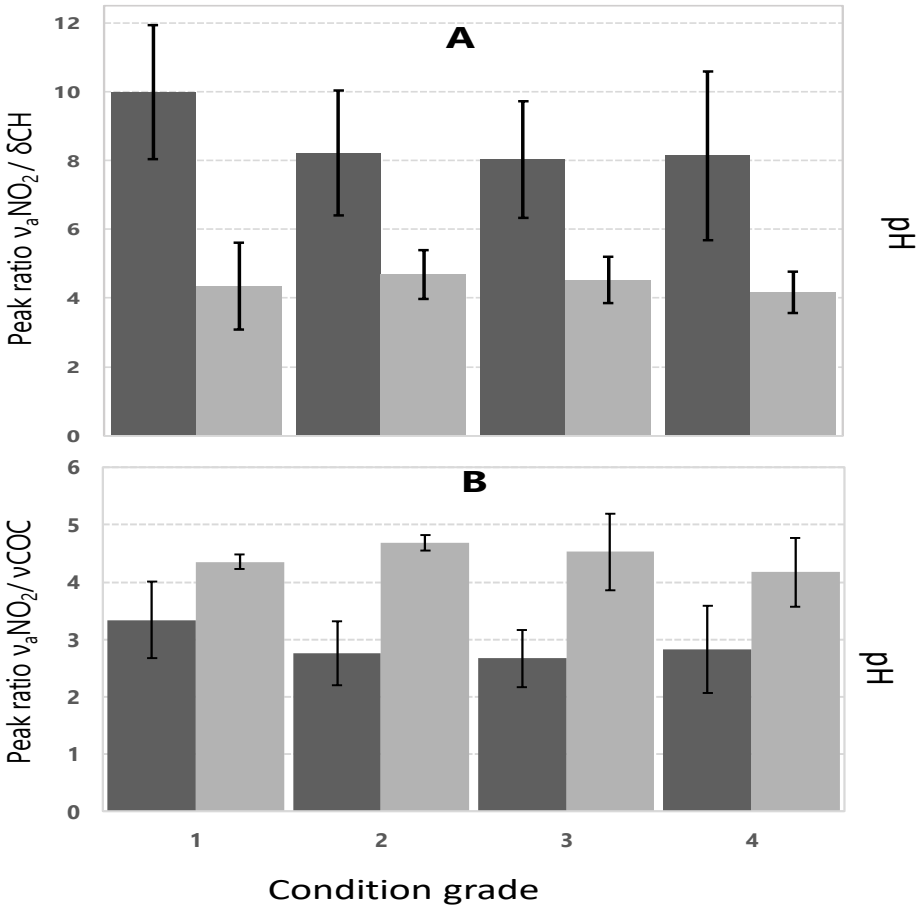


Figure 6.29 – Results from the VA and MA correlation. Peak ratios Infrared peaks ratios ν_aNO_2 / δCH and ν_aNO_2/ νCOC (dark grey bars) and pH averages and SD (light grey bars). Values are averages of set of case studies per condition grade.

Despite of the decrease of the peak ratios observed, when organizing data by VA condition grades attributed to case studies is possible to conclude that there is no correlation between VA and MA since the peak ratio values obtained are not significantly different (not exclusive). Additionally, in some situations, there are no differences at all. Regarding pH, the average values obtained per condition grade for each set of case

studies are identical. Therefore, it was concluded that there is no correlation between visual assessment and molecular assessment (MA)[114].

6.3.2 Molecular assessment of the case studies from DGEMN collection

As previously said, this collection was selected with the aim to assess film-based negatives with CN support resulting from a different production context. In this way, it was aimed to compare the results accomplished with the molecular assessment of DGEMN collection with the previous collection scoped in order to acknowledge the condition of these historical collections. Except for the analysis performed for identification of chemical compounds on the image layer, for the study of DGEMN collection, the methodology followed the steps previously described in the previous section. In this way, the μ-FTIR, pH and hardness (Shore A) results are disclosed along with a discussion of the results that are simultaneously compare with data obtained with the assessment of ECC collection.

Based on the presence of the characteristic stretching absorptions associated to nitrate group, ONO_2, at 1655 cm^{-1}; 1282 cm^{-1}; 841 cm^{-1},and stretching vibrations of C-O-C ring at 1160 cm^{-1}, 1069 cm^{-1}, 1003 cm^{-1}, the μ-FTIR analysis allowed to conclude that all negatives selected from DGEMN collection have a cellulose nitrate base (Fig. 6.30)[115]. In a total set of four case studies (with the index ref. fD 17681, fC 6733, fC 6734 and DGEMN 18_14), peaks attributed to phthalate and phosphate plasticizers were found. Moreover, a combination of camphor, and phthalate and phosphate plasticizers was found in only one of these films (index ref. fD 17681).
Figure 6.30 depict the infrared spectra of five case studies from DGEMN collection, namely fA 91 (a), fC 1532 (b), fB 4732 (c), fB 4861 (d) and fD 17602 (e)[116], with formats raging between 60mm and 18x24 cm[117].

[114] For detailed information about each case study, see Table V.1 in Appendix V.
[115] Infrared peaks assignment for cellulose nitrate are depicted in Table IV.1, in Appendix IV.
[116] The case studies are identified according to the indexation designations and numbers attributed by the conservators from the SIPA-DGPC archive.
[117] The indexation references and numbers were established by the institution that held the collection and are related with negatives' formats (negatives with fD reference have a 35mm to 60mm format, those with fC have 9x12 cm format, fB is attributed to 10x15 and 13x18 cm format and, for last, the fA designation is attributed to larger formats,18x24 cm).

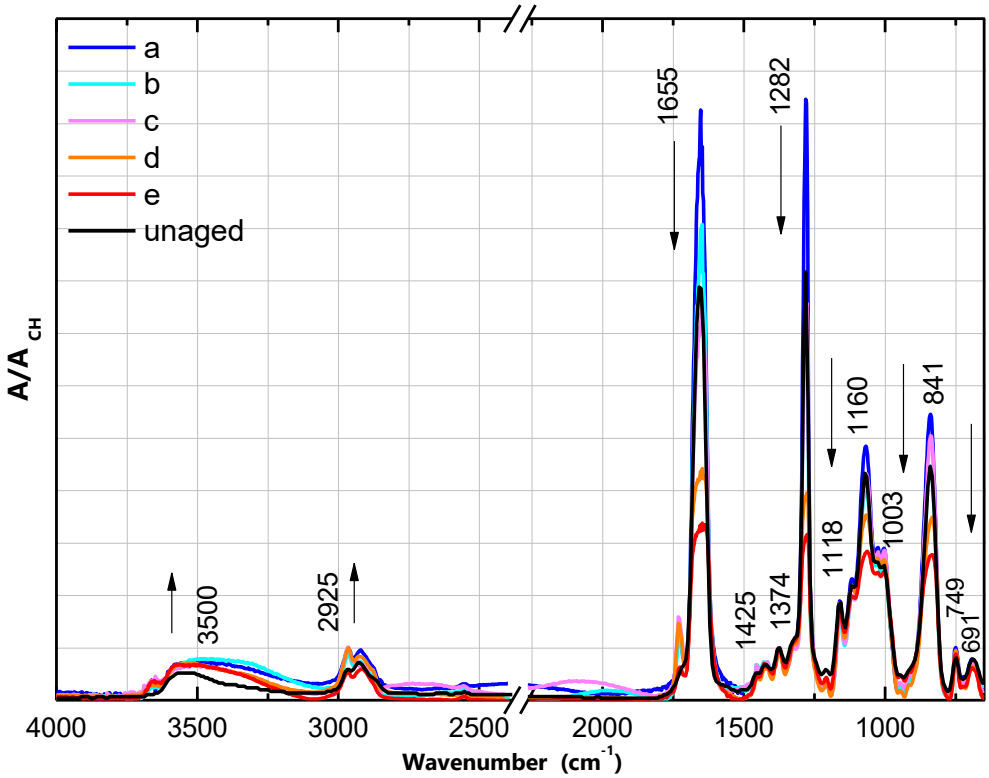


Figure 6.30 – Infrared spectra of five case studies from DGMN collection and a cellulose nitrate unaged film (black), with absorptions normalized for CH bending (1374 cm^{-1}). Case studies: fA 91 (a), fC 1532 (b), fB 4732 (c), fB 4861 (d) and fD 17602 (e).

As for ECC collection, the FTIR spectra obtained for case studies from DGEMN collection show minor increase of the intensity in the O-H stretch region, with intensities ranging from 0,5 (minimum) to 1,4 (maximum). Moreover, a shift of the peak at 3570 cm^{-1} to lower wavenumbers (to 3430 cm^{-1}) and an insignificant broadening of the peak detected in a small set of samples (9) were observed (Fig 6.30). In the same way, minor increases on the intensity of the C-H stretching absorptions at 2960 and 2915 cm^{-1} are noticed. The molecular assessment of the case studies from DGEMN collection was performed by following the decrease of the intensity (absorption) determined with the $\nu_a NO_2$ / δCH and $\nu_a NO_2$/ νCOC peak ratios. The comparison of the ratios was carried out per formats, thus several tables summarizing the ratios obtained are presented (Tables 6.4 to 6.7). Additionally, pH and hardness results per set of case studies organized per formats are also presented. The results disclosed will follow the formats sequence from the smaller (35mm) to the larger format (18x24 cm).

In Figure 6.31, two case studies with 35mm format from the DGEMN collection are presented.

Figure 6.31 – Overall view of two nitrate-based negatives with 35mm format from the DGEMN archive. Left: index ref. DGEMN 14, VA condition 2. Right: index ref. DGEMN 227, VA condition 3. © DGPC-SIPA/ credits Élia Roldão.

In Table 6.4, infrared peak ratios (absorptions intensities), and pH and hardness (Shore A) measurements (averages, SD) per case study with 35mm from DGEMN collection are presented. Data was organized according to the highest for the lowest peak intensity for $\nu_a NO_2$ / δCH and $\nu_a NO_2$/ νCOC.

Table 6.4 – Case studies from DGEMN collection with 35mm format: visual assessment (VA) classification, infrared peak ratios (absorptions intensities), pH and hardness (Shore A) measurements (averages, SD). Infrared spectra normalized for CH bending (1374 cm^{-1}).

VA	Samples	$\nu_a NO_{2\ 1655\ cm^{-1}}$ / $\delta CH_{1374\ cm^{-1}}$	$\nu_a NO_{2\ 1655 cm^{-1}}$ / $\nu COC_{1160\ cm^{-1}}$	pH	Hardness (Shore A)
4	348	9.1	4.2	6.3 ±0.1	99.8±0.4
3	1	7.6	3.5	6.3±0	99.8±0.4
3	227	5.5	2.5	6.3±0	99±0.4
4	118	4.7	2.1	6.4±0.1	99.8±0.4
2	14	4.6	2.1	6.4±0.1	99.4±0.5

The peak ratios (absorptions intensities), and pH and hardness (Shore A) measurements are in the range of peak ratio values obtained for ECC collection[118]. Again, the average hardness values obtained do not vary, indicating that possibly this technique is not sensible to changes on cellulose nitrate-based films or there is no loss of the physical properties within this set of case studies. Moreover, within this set of negatives with 35

[118] Summary of data obtained for case studies from ECC collection (maximum-minimum): $\nu_a NO_{2\ 1655\ cm^{-1}}/\delta CH_{1374\ cm^{-1}}$ and $\nu_a NO_{2\ 1655cm^{-1}}/\ \nu COC_{1160\ cm^{-1}}$ ratios obtained were 14 and 4.1; and 4.8 and 1.4, respectively; average pH values and SD 5.8±0.1 and 3.2±0.2; average hardness (Shore A) values and SD, 99±0 and 97.4±1.8.

mm format, the pH values obtained are identical (with negligible SD). The consistency of the pH results obtained for the 35mm set may be correlated with the lack of the anti-curl layer. For this set, the average pH values express the measurement of the nitrate base rather than the gelatine coating layer. These results led questioning 'Do the pH measurements obtained for the case studies from ECC collection reflect the protective and amphoteric behaviour of gelatine?'. This issue will be discussed again at the end of this section, after having presented the results obtained for the remaining sets of negatives from the DGEMN collection. Regarding VA and MA correlation, according to the results acquire for 35mm set, there is not a straightforward correlation between both assessments.

Concerning the medium formats (60mm), fourteen case studies were selected. In Figure 6.32, two case studies with different condition grade are presented.

Figure 6.32 – Overall view of two case studies with 60mm format from the DGEMN archive: index ref. fD 17682 in VA condition 1 (a) and fD 17602, VA condition 5 (b). © DGPC-SIPA/ credits Élia Roldão.

The peak ratios (absorptions intensities), average pH and hardness values obtained for case studies with 60mm format from DGEMN collection are summarized in Table 6.5.

Table 6.5 – Case studies from DGEMN collection with 60mm format: visual assessment (VA) classification, infrared peak ratios (absorptions intensities), pH and Hardness (Shore A) measurements (averages, SD). Infrared spectra normalized for CH bending (1374 cm^{-1}).

VA	Samples	ν_aNO_2 1655 cm^{-1} / $\delta CH_{1374\ cm^{-1}}$	ν_aNO_2 1655cm^{-1} / $\nu COC_{1160\ cm^{-1}}$	pH	Hardeness (Shore A)
3	fD 17681	15.6	4.3	6.3±0.2	99.4±0.5
4	fD 17612	9.4	2.6	4.8±0.2	99.8±0.4
4	33 B	8.9	2.5	6.3±0	100±0
1	fD 17682	8.8	2.4	5.5±0.3	99.2±0.4
4	15_150	8.6	2.4	6.3±0.1	100±0
3	fD 17603	8.1	2.2	4.3±0.2	99.2±0.4
4	PAG 30	6.9	1.9	6.3±0.1	99.2±0.4
4	fD 17675	6.1	1.7	4.2±0.1	99.6±0.5
4	57	5.6	1.5	6.1±0.1	99.8±0.4
3	fD 17601	5.4	1.5	4.6±0.1	99.4±0.5
3	33	4.9	1.3	6.1±0.1	100±0
4	fD 17613	4.7	1.3	4.9±0	99.6±0.5
4	fD 17602	3.4	0.9	4.5±0.1	99.6±0.4

Comparatively with data presented for the set of negatives with 35mm format , a wider range of ν_aNO_2 / δCH and ν_aNO_2/ νCOC ratios was seen. Comparatively with peak ratios obtained for the set of case studies from ECC collection, in the set of case studies with 60mm format from DGEMN collection, two peak ratios were obtained, extending the maximum and minimum values collected till now in the assessment of cellulose nitrate-based negatives scoped. The maximum peak ratio obtained (15.6) may be related with the combination of camphor, phthalates and phosphates (plasticizers). As previously said, the combination of these plasticizers was identified by FTIR spectroscopy analysis of the case study with the index nº fD 17681. In an opposite situation, case study fD 17602 (Fig. 6.32b) shows the lowest ratio found in the set of case studies from ECC and DGEMN collection, indicating the possible quantification of the decay of the film. Additionally, the overall pink hue in the anti-halation layer (commonly associated with plastic negatives with a CA base) was noticed, indicating changes of the pH that might result from the chemical decay of the film support. However, and unlike the set of negatives with 35mm format, the average pH values obtained for the set of case studies with 60mm format are discrepant and do not show a clear correlation between the μ-FTIR results obtained from the analysis of the support. Nevertheless, the average pH values obtained may be reflecting the condition of the gelatine layer.

Regarding hardness, overall the hardness values obtained do not vary significantly and are in the range of the values collected for the previous sets, allowing suggesting that also these films and formats maintain their mechanical strength.

The following Tables 6.6 and 6.7, summarize data collected for nitrate-based sheet films with 9x12 cm, 10x15 and 13x18 cm, as lastly for 18x24 cm formats, respectively, from DGEMN collection.

In Fig. 6.33, two case studies with 9x12 cm format from DGEMN collection are shown. Discoloration (general or localized) and loss of gelatine layers were the degradation signs found in the two case studies presented there.

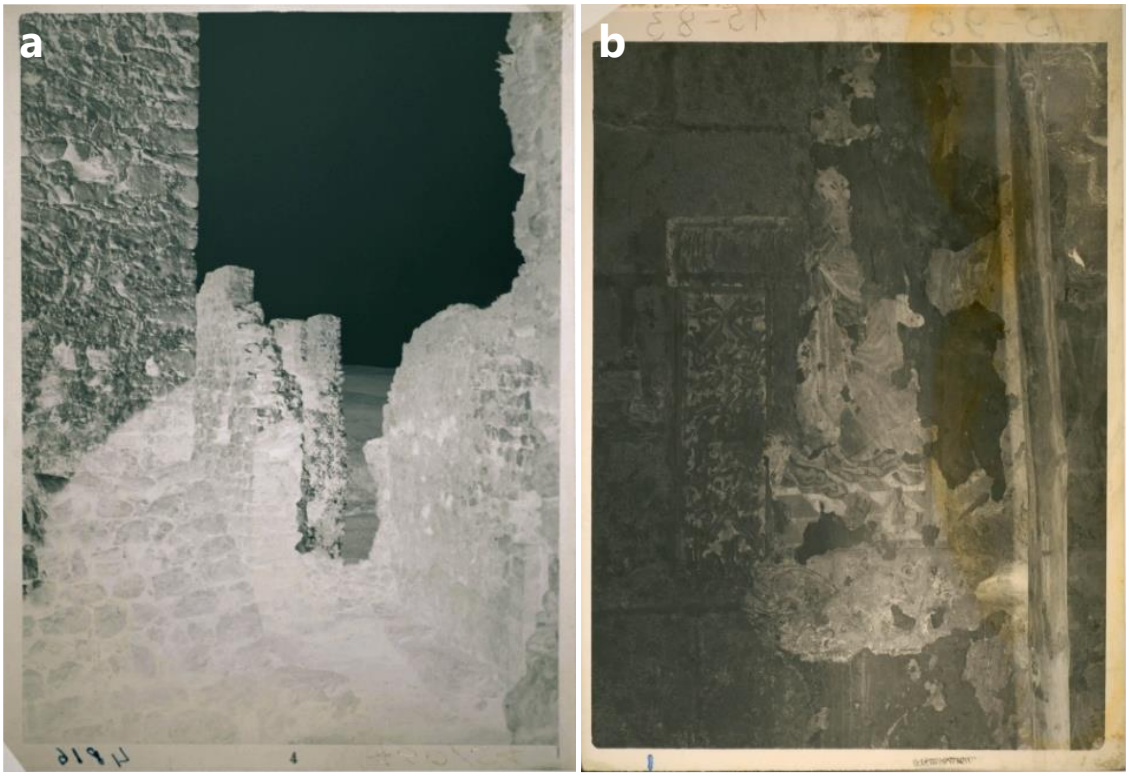


Figure 6.33 – Overall view of two case studies with 9x12 cm format from the DGEMN archive: fC 6744, VA condition 4 (a) and DGEMN 15_127, VA condition 4 (b). © DGPC-SIPA/ credits Élia Roldão.

Table 6.6 – Case studies from DGEMN collection with 9x12 cm format: visual assessment (VA) classification, infrared peak ratios (absorptions intensities), pH and Hardness (Shore A) measurements (averages, SD). Infrared spectra normalized for CH bending (1374 cm^{-1}).

VA	Samples	$\nu_a NO_2$ 1655 cm^{-1} / δCH_{1374} cm^{-1}	$\nu_a NO_2$ 1655cm^{-1} / νCOC_{1160} cm^{-1}	pH	Hardeness (Shore A)
5	18_14	12.7	6.8	6.6±0.1	99.8±0.4
3	fC 1546	10.8	5.7	6 ±0.2	99.8±0.4
3	fC 1532	9.0	4.8	5.4±0.6	99.6±0.5
4	fC 6739	8.3	4.4	4.3±0.1	99.8±0.4
4	15_127	7.8	4.1	3.4±0.2	99.6±0.5
4	fC 6734	7.1	3.8	6.6±0.2	100±0
2	fC 6742	6.9	3.7	5.3±0	99.6±0.5
1	fC 6755	6.2	3.3	5.7±0.1	99.8±0.4
3	fC 1543	5.9	3.2	5.8±0.4	99.4±0.5
4	fC 6733	5.1	2.7	5.9±0	99.8±0.4
4	fC 6744	4.3	2.3	5.1±0.4	99.4±0.5

The peak ratios calculated for this set of case studies are within the range of values obtained for case studies from ECC collection. Moreover, in this set of selected items, three (index nº 18_14, fC 6733 and fC 6734) exhibit peaks attributed to phthalate and

phosphate plasticizers and lack the peak at the C=O (1733 cm^{-1}) region attributed to camphor. A closer look to the peak ratios obtained allow to conclude that the highest value obtained is again related to a case study with phthalate and phosphate plasticizers in its composition. Regarding the μ-FTIR analysis and the pH and hardness values, the data gathered for case studies with 9x12 cm format, are identical to the results obtained for the previous sets of case studies from ECC and DGEMN collection.

Concerning the case studies from DGEMN collection with large formats (10x15 and 13x18, 18x24 cm), the results obtained are summarized in Tables 6.7.

The results summarized in Tables 6.7 indicate the same behaviour and conclusions described in the discussion of the results performed for the previous sets.

Table 6.7 – Case studies from DGEMN collection with 10x15 and 13x18 cm formats: visual assessment (VA) classification, infrared peak ratios (absorptions intensities), pH and Hardness (Shore A) measurements (averages, SD). Infrared spectra normalized for CH bending (1374 cm^{-1}).

VA	Samples	$\frac{\nu_a NO_2\ 1655\ cm^{-1}}{\delta CH_{1374\ cm^{-1}}}$	$\frac{\nu_a NO_2\ 1655 cm^{-1}}{\nu COC_{1160\ cm^{-1}}}$	pH	Hardness (Shore A)
10x15 and 13x18 cm format					
5	17_8	10	5.8	4.2±0.1	99.4±0.6
4	fB 4869	9.7	5.6	4.1±0.1	99.4±0.5
3	fB 4871	9.2	5.3	5.2±0.4	99.2±0.5
3	fB 4742	8.6	5.0	5.4±0.2	99.2±0.5
3	fB 4760	8.4	4.8	6.2±0.1	99.4±0.5
4	fB 4749	8.3	4.8	4.1±0	100±0
1	fB 4732	7.6	4.4	6.3±0.1	99.4±0.6
2	fB 4759	7.5	4.3	5.6±0.2	99.6±0.6
3	fB 4734	7.5	4.3	5.4±0.1	99.4±0.6
4	fB 4872	7.1	4.1	4.1±0.1	99.4±0.6
3	fB 4746	5.8	3.3	5.8±0.1	100±0
5	fB 4866	5.2	3.0	4.7±0.1	99±0
4	fB 4748	4.9	2.8	5.1±0.1	99.4±0.5
5	fB 4861	4.4	2.5	6.4±0.1	99.6±0.5
18x24 cm format					
2	fA 91	11.3	5.9	6.2 ±0.1	99.6±0.5
5	fA 114	10.9	5.7	4.9 ±0.3	99.8±0.4
3	fA 110	9.8	5.2	6.1 ±0.1	99.6±0.5
3	fA 93	6.5	3.4	6 ±0.3	99.2±0.4
4	fA 107	6.0	3.2	5.5 ±0.2	99.8±0.4
3	fA 113	5.0	2.7	5.6±0.1	99.8±0.4

μ-FTIR, pH and hardness results are identical to the results obtained for the previous sets of case studies.

To confirm that the obtained results will be the expected ones for collections of nitrate-based negatives, it was necessary to look for negatives that represented a situation of irreversible loss of the objects. From Mário Novais collection exemplars od such situation were found. The results of the analyses carried out are presented in the following section.

6.3.3. Molecular assessment of a case study from Mário Novais collection

The case studies from MN collection are completely lost[119]. The negatives, 18x24 cm format, are stick to each other, with marked yellowing-brownish hue, noxious nitric acid odour, absence of image and brittle (see Fig. 6.12).

Fig. 6.34 depict the FTIR spectra obtained by analysing the case study from MN collection against a CN standard.

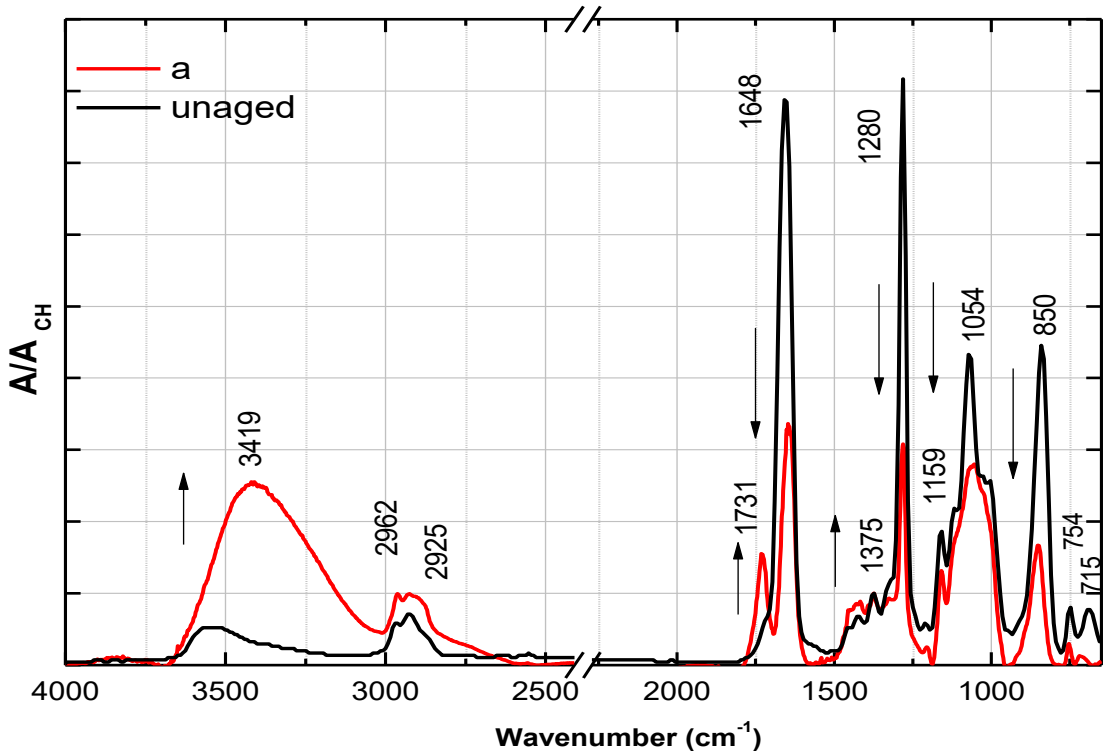


Figure 6.34 – Infrared spectra of the case study from MN collection (a) and a cellulose nitrate unaged film (black), with absorptions normalized for CH bending (1374 cm^{-1}).

In the O-H stretching absorption, an increase of the intensity (up to 2,6) and shift of the peak to lower wavenumbers was observed. Additionally, an increase of the absorption intensities and loss of the resolution of peaks in C-H stretching region (at 2962 and 2915 cm^{-1}) was also observed. Moreover, a decrease on the absorption intensities in the

[119] These case studies belong to collection CFT003 - Mário Novais, from Biblioteca de Arte, Fundação Calouste Gulbenkian.

regions attributed to NO stretching at 1655, 1282 and 841 cm^{-1} were detected. The peak ratios $\nu_a NO_{2\ 1655\ cm^{-1}}$/ $\delta CH_{1374\ cm^{-1}}$ and $\nu_a NO_{2\ 1655\ cm^{-1}}$/ $\nu COC_{1160\ cm^{-1}}$ obtained for the case study from MN col. are 3.4 and 2.5, respectively. Comparing these results with the previous, it is was concluded the ratios obtained for case study from MN col. are identical to many of those obtained for case studies from ECC and DGEMN collection. Thus, it was questioned why does the case study from MN col. be completely destroyed when the other case studies are still, apparently, in Fair condition? This issue became even more interesting when pH measurements were carried out. According to the results obtained, the average pH value obtained for MN sample is the lowest obtained (1.3±0.2) for the all set of case studies scoped. However, due to the reduced dimension of the sample, it was not possible to perform hardness measurements that could shed light in the physical decay of this specimen.

More doubts were raised when a closer observation of the obtained $\nu_a NO_{2\ 1655\ cm^{-1}}$/ $\nu COC_{1160\ cm^{-1}}$ ratio indicates that the lowest ratio obtained correspond to case study fD 17602 from DGEMN collection rather than for the case study from MN collection. A closer observation of the OH and C=O (peaks at 1740 and 1655 cm^{-1}) regions was performed by fitting with a Gaussian function (Table 6.8).

Table 6.8 – Case studies fD 17602 and MN: fitting parameters for OH and C=O stretching (1740 and 1655 cm^{-1}), correlation coefficient (ρ), peak centre (μ), area of the peak (A), full width at half maximum (σ) and peak height (H). Spectra normalized for δC-H at ~1374 cm^{-1}.

Sample	OH				C=O (NO $_{1655\ cm-1}$)				Camphor (1740 cm^{-1})			
	ρ	μ	A	H	ρ	μ	A	H	ρ	μ	A	H
fD 17602	0,92	3464.07	304,71	0,74	0,95	1652,94	302,57	3,8	0,95	1723.4	23.12	0,61
MN	0,94	3373.0	898,43	2,41	0,99	1646.34	166.41	3.4	0,97	1728.8	65.56	1.38

In Table 6.8 evident differences are confirmed. According to the results obtained, the major differences are found in the areas of the peaks considered. Moreover, the intensity of the peaks at the O-H stretching and camphor allowed to assess the film decay and to suggest that the severe degradation recorded for case study from MN col. results from partial loss of nitrate groups and increasing formation of polar groups (e.g. O-H) that are affecting the physical properties of the polymer. Additionally, the intensity of the peak associated to camphor is probably related with the formation of degradation products (ketones, NO_x).

These results agree with the typical decay of cellulose nitrate-based negatives (denitration>sublimation of camphor>formation of degradation products>chain-scission) described in the literature (Edge et al. 1990; Quye et al. 2011). Given the lack of historical information regarding the photographer method and past storage, it is not

possible to suggest if the severe decay observed for case study from MN collection results from intrinsic degradation (specific chemical composition) or external degradation factors (improper storage). Taking into consideration the formats of the two case studies compared, is was not excluded the fact that thickness (which, as previously described in Chapter 2, is related with format) could contribute for the different degradation pathways found. As previously discussed,[120] nitrate-based negatives with greater thickness (usually sheet films) retain the degradation products in the bulk of the film. This behaviour can lead to a greater extent of degradation. Comparatively, roll film (small formats with thinner layers) allow greater release of degradation products. Nevertheless, for case studies with the same format from DGEMN collection, severe degradation was not found. The reduced number of samples do not allow to conclude the reason for such difference on the behaviour, therefore additional investigation on this topic should be carried out.

To support the findings obtained with naturally aged negatives, an artificial ageing was carried out in which a CN reference and four types of photographic film (one sheet and three roll films) and one motion picture film were submitted to constant temperature (80ºC) and relative humidity (90%)[121] (the results are presented in Appendix VI). The results confirmed that is possible to assess the film decay by measuring hardness since, hardness decreases along with extensive decrease of nitrate groups. It was also observed that pH decreases along with the increasing of the molecular decay of CN film supports. A significative decrease of hardness and pH was obtained for sheet film and motion picture film, while minor changes were observed for the other samples. Additionally, according to the results obtained, sheet film and motion picture film degraded faster than the other roll films examined, which kept the chemical and physical behaviour stable for more time.

6.3.4 Molecular assessment of San Payo collection

'San Payo ... is one of the examples of the good surprises that Portuguese photography can reserve for contemporaries [...] (Barreto 1995, 22)

San Payo was not only a good surprise for Portuguese photography, it was also a good surprise for this study. The surprises came along with the μ-FTIR results that allowed to characterize the film supports of the 190 case studies selected. As it is going to be explained in this section, these results confirm that the methods indicated by Portuguese conservators may not provide accurate identification, especially when considering negatives lacking historical information (e.g. dating), technical information (brand, producer, typology) or signs of degradation (absence or presence). The San Payo's film

[120] For more information about this topic see section 2.5.1.1, page 61.
[121] See Appendix VI.

collection allowed to detect the risks, which support the review and contributions for film identification and assessment guidelines.

Based on the FTIR characteristic peaks attributed to cellulose nitrate and cellulose acetate (features already described in the beginning of the section 6.3.3), 23 case studies with cellulose nitrate-base were identified. The remaining 174 case studies have a cellulose acetate or cellulose acetate butyrate support. Regarding the cellulose nitrate-based negatives, the formats of the negatives ranged between 35mm format (1 specimen), 60mm (19 specimens) and 10x15 and 13x18 cm (3 specimens). The molecular assessment followed the methodology previously presented. From the set of case studies with cellulose nitrate-base, in Tables 6. 9 the visual assessment (VA), peak ratios $\nu_a NO_{2\ 1655\ cm^{-1}}$ / $\delta CH_{1374\ cm^{-1}}$ and $\nu_a NO_{2\ 1655\ cm^{-1}}$/ $\nu COC_{1160\ cm^{-1}}$, and average pH and Hardness (Shore A) measurements are presented.The μ-FTIR analysis allowed to distinguish cellulose nitrate-based negatives with different plasticizer formulations, some only with camphor (10 specimens), a set with phthalates and/or phosphate (12) and a single case study with the combination of both (camphor and phthalates and/or phosphate).

Table 6.9 - Cellulose nitrate-based samples with 35mm (bold), 60 mm and 10x15 and 13x18 cm formats from San Payo collection: visual assessment (VA) classification, infrared peak ratios (absorptions intensities), pH and hardness (Shore A) measurements ±SD. Infrared spectra normalized for CH bending (1374 cm^{-1}).

VA	Samples	$\frac{\nu_a NO_{2\ 1655\ cm^{-1}}}{\delta CH_{1374\ cm^{-1}}}$	$\frac{\nu_a NO_{2\ 1655 cm^{-1}}}{\nu COC_{1160\ cm^{-1}}}$	pH	Hardness (Shore A)
35mm and 60mm format					
3	SP 561	12.2	4.1	5.9±0.1	99±0
2	SP 558	12.0	4.0	5.9±0.1	99±0
3	SP 560	11.9	4.0	5.7±0.1	98.8±0.4
2	SP 569	11.6	3.9	5.8±0	99±0
3	SP 563	11.2	3.7	5.5±0.3	99±0
3	SP 573	10.3	3.4	4.3±0.2	99±0
3	SP 557	10.2	3.4	5.9±0.2	99±0
1	**SP 549**	10.1	3.4	5.7±0.1	99±0
4	SP 571	9.9	3.3	5.6±0.1	99±0
2	SP 562	9.6	3.2	5.5±0.1	99±0
3	SP 568	9.4	3.1	5.5±0.1	99±0
3	SP 574	9.4	3.1	4.9±0.3	99±0
3	SP 605	8.7	2.9	5.6±0.1	99±0
3	SP 564	8.6	2.9	5.7±0.2	99±0
3	SP 565	8.5	2.8	5.8±0.1	99±0
2	SP 559	8.5	2.8	5.8±0	99±0
3	SP 566	8.4	2.8	4.7±0.7	99±0
3	SP 572	8.1	2.7	5.5±0.1	99±0
4	SP 604	7.9	2.6	5±0.2	99±0

(cont.)					
10x15 and 13x18 cm format					
3	SP 505	10.6	3.5	5.1±0.2	99±0
3	SP 331	8.3	6.1	6.2±0.1	99.4±0.5
3	SP 13	6.8	5.0	5.1±0.1	99±0
3	SP 97	5.7	4.2	5.1±0.6	99±0

Overall the results obtained agree with data accomplished for cellulose nitrate-based negatives from the ECC and DGEMN collections. Comparatively with the other sets, higher average pH values were consistently found for case studies from SP collection, especially for samples with 60mm format with phthalate and/ phosphate plasticizers with average pH ~6 (e.g. samples SP 557, SP 558, SP 559, SP 560, SP 561).
In order to correlate the peak ratios $\nu_aNO_{2\ 1655\ cm^{-1}}$/ $\delta CH_{1374\ cm^{-1}}$ and $\nu_aNO_{2\ 1655\ cm^{-1}}$/ $\nu COC_{1160\ cm^{-1}}$ with the average pH values obtained, the Pearson correlation coefficient was determined. For this case, negligible correlations (0.289 and 0.282) and *p*-values of 0.1795 and 0.1916 of ratios and pH were obtained. Since plastic negatives are composite materials, all the compounds present in their composition may be contributing for stability or decay of the polymer and, consequently, for its pH. Thus, based on the results obtained for the sets of case studies with cellulose nitrate base, three plausible reasons may be suggested for this phenomenon i) gelatine is scavenging the acids formed in first stages of CN film decay, ii) plasticizers in part are also scavenging and/or contribute for a pH equilibrium of plastic negatives, iii) the spectral changes and ratios determined do not reflect the chemical decay of CN supports and then a negligible correlation between those and pH is obtained. For an in-depth understanding of gelatine and plasticizers role on the stability of cellulose nitrate-based negatives, future work must be done. Concerning hardness, the insignificant changes obtained with hardness measurements allow to conclude that these negatives are in Good to Fair condition.

Regarding the cellulose acetate-based negatives, by μ-FTIR analysis it was possible to distinguish cellulose acetate and cellulose acetate butyrate supports. The typical peaks attributed to CA polymer are present, the C=O stretching (at 1751 cm^{-1}), C-C-O stretching (at 1234 cm^{-1}) and O-C-C stretching (between 1049-1051 cm^{-1}) (Edge et al. 1989; Littlejohn et al. 2013; Richardson et al. 2014; Schilling et al. 2010; Giachet et al. 2014). Additionally, peaks in the methyl stretching vibration regions at 2875, 1370 and 1273 cm^{-1}, and a peak at c. 1088 cm^{-1} allow to identify cellulose acetate butyrate (Schilling et al. 2010). Additional peaks at circa 1589,1489, 1278, 1187, 1124, 1006, 960 and 744 cm^{-1} are attributed to plasticizers (phthalates and phosphates) (Schilling et al. 2010; Rambaldi et al. 2014). Figure 6.35 depict the FTIR spectra of cellulose diacetate and cellulose triacetate model films (d and e) and case studies from SP collection for which the support was identified as CTA, CAB, and CA (a, b, and c).

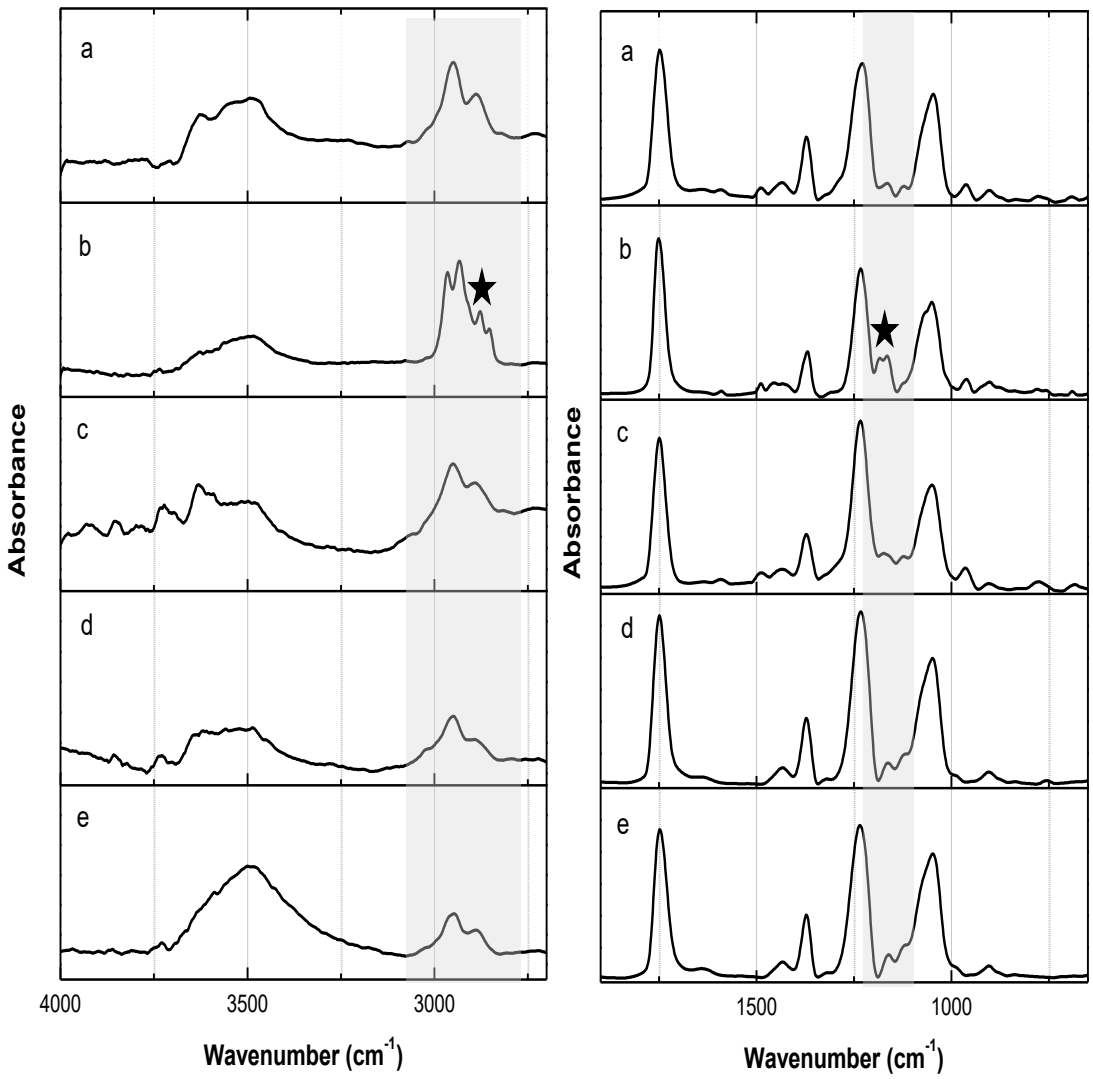


Figure 6.35 - FTIR spectra of cellulose diacetate and cellulose triacetate model films (d and e) and case studies from SP collection with CTA, CAB, and CA supports. CTA: SP 547 (a). CAB: SP 201 (b, ★). CA: SP 194 (c). Spectra normalized for C-O-C stretching (1051 cm^{-1}).

The grey areas within Fig. 6.35 indicate the two main FTIR regions that allow to distinguish the polymers from CA family. As highlighted (with a black star), on CAB polymer the different shape and intensity of the peaks in the methyl stretching vibration peaks, along with an additional peak at 2875 cm^{-1}, is observed. Additionally, two peaks at ~1188 and 1164 cm^{-1} are also attributed to CAB polymer. These spectral features result from the use of esterifying acids with high number of carbon atoms such as butyric acid, distinguishing CAB from the remaining family of CA polymers.

Additionally, minor differences in the shape of the peaks and absorption intensities in the O-H (3450 cm^{-1}), C-H (3000 – 2840 cm^{-1}) and C=O_{Ac} (1746 cm^{-1}) stretching regions for CA and CTA are emphasized in the literature (Giachet et al. 2014) . The peaks shape and intensities reflect the degree of acetylation, however, due to the assorted formulation used throughout decades, these differences may not be enough to distinguish CDA and

CTA by FTIR spectroscopy. In fact, this is even an arduous task when considering the hydrolytic decay of CA historical films (Giachet et al. 2014).

Regarding the identification of historical films scoped in this study, the identification of CA's and CAB film supports relied mostly on spectral features found in the methyl (3000 – 2840 cm^{-1}) and C-O-C (1070-1150 cm^{-1}) stretching regions (Fig. 6. 35, b, ★). Thus, by FTIR spectroscopy, sixty-two specimens with a cellulose acetate butyrate support and eighty-eight with a cellulose acetate support were identified. Case studies with a CAB support are all sheet films. Concerning negatives with CA support, the type of film support is not restricted to a format, it ranges between roll film (60mm) to sheet film (up to 13x18 cm^{-1}).

The decay of CA polymer, known as 'Vinegar syndrome', is regarded for, one deacetylation (accelerated by moisture, acids or alkaline products) and formation of acetic acid, followed by acid hydrolysis and consequent chain-scission (Edge and Allen 1992). Thus, from the decay of CA's polymers, a decrease of acetyl groups and growth of hydroxyl groups is expected (Edge et al. 1989; Littlejohn et al. 2013; Giachet et al. 2014).

In Figure 6.36 the spectral changes found in a set of five cellulose acetate-based negatives from SP collection are presented, showing the typical decay of CA polymers.

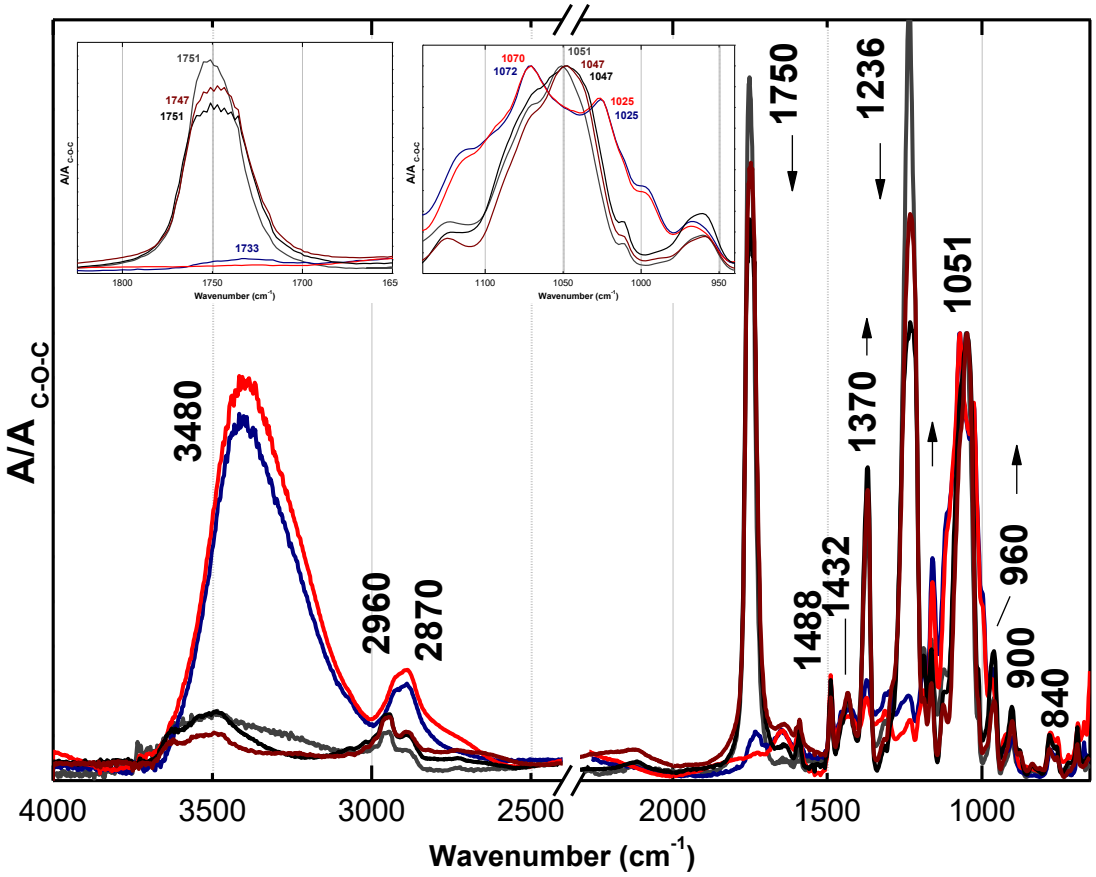


Figure 6.36 – Infrared spectra of five cellulose acetate-based negatives in different degradation condition. Insets: detail of the C=O stretching region from 1825 to 1650 cm^{-1} (left) and detail of C-O-C stretching region from 1140 to 940 cm^{-1}. Spectra normalized for C-O-C stretching (1051 cm^{-1}).

As shown in Fig. 6.36, spectral changes in O-H, $C=O_{Ac}$, C-O-C stretching regions allowed to assess the condition of cellulose acetate-based negatives. A significant increase of the peak at ~3480 cm^{-1} along with total loss of intensity in the $C=O_{Ac}$ and C-O stretching regions (1751 and 1232 cm^{-1} respectively) is observed for case studies in severe condition (blue and red spectra). The extension of the deacetylation is clearly visible in the detail of the C=O stretching region, in which a broadening and shifting of the peaks is perceived (Fig. 36, inset at left). A closer observation of the O-H and C=O was made for five samples with conditions ranging from Good to Severe, by fitting a Gaussian function. The results obtained are presented in Table 6.10.

Table 6.10 – Values of peak centre (μ), area (A), peak width at half maximum (ρ) for the hydroxyl and carbonyl stretching regions (Gauss function) for cellulose acetate-based negatives.

Sample	O-H			C=O		
	μ	A	ρ	μ	A	ρ
SP 43	3459	30.63	0.87	1749	53.44	0.99
SP 272	3507	19.32	0.95	1747	55.46	0.98
SP 194	3515	95.99	0.87	1746	53.98	0.99
SP 380	3380	255.84	0.96	1743	10.11	0.95
SP 816	3361	333.33	0.97	---	---	---

The results presented in Table 6.10 summarize the values obtained for the all set of negative with a CA support, pointing out for the enlargement of the area of the peak in the O-H stretching region for samples with visible signs of degradation. At the same, in this region, a peak shift is observed. For samples severely degraded, significant changes are observed in the region attributed to the C-O-C stretching vibration indicating changes in the pyranose ring (Fig. 6.36, inset at right).

Moreover, in the carbonyl region the spectral changes are noticed with peak shift and decrease of the intensity (absorption). Taking that in consideration, in order to assess the molecular decay of all samples with CA and CAB support, the intensities of the peaks in the O-H, C=O and C-O stretching regions were rationed against the C-H peak (1369 cm^{-1}), which remains moderately constant in CA (Littlejohn et al. 2013). For the sake of clarity of the presentation and discussion of the results obtained, the ratios calculated for CA and CAB film supports were compiled and presented together to allow a comparison of the acquired for both.

In Figure 6.37 the O-H/C-H peak ratio (absorption intensities) for case studies with CAB and CA supports, as well as CDA and CTA model films is presented.

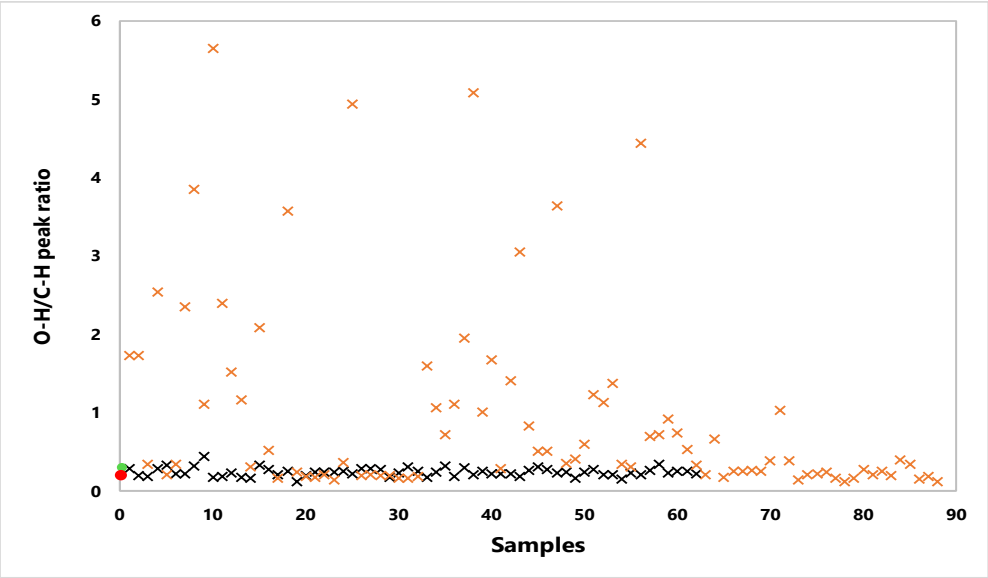


Figure 6.37– O-H/C-H peak ratio on negatives with CAB (black) and CA (orange) supports, and CDA (green dot) and CTA (red dot) model films. Spectra normalized for C-O-C stretching (1051 cm^{-1}).

Based on the O-H/C-H peak ratio, it was expected to evaluate the extension of hydroxyl groups formed per each sample. According to data presented in Fig. 6.37, for negatives with a CAB support insignificant differences (ratios ranging between 0.1 and 0.4) are observed. Comparatively, for negatives with a CA support, a significative variation of the ratios (ranging from 0.1 to ~6) was obtained. The variability found for the set of case studies with CA support, may be correlated with DS and acetyl content or due to decay (deacetylation and chain scission). To complement these results, C=O/C-H and C-O/C-H peak ratios were calculated with the aim to assess the loss of acetyl groups per sample. In Fig. 6.38 (a,b), C=O/C-H and C-O/C-H peak ratios obtained for samples with CAB and CA supports are presented.

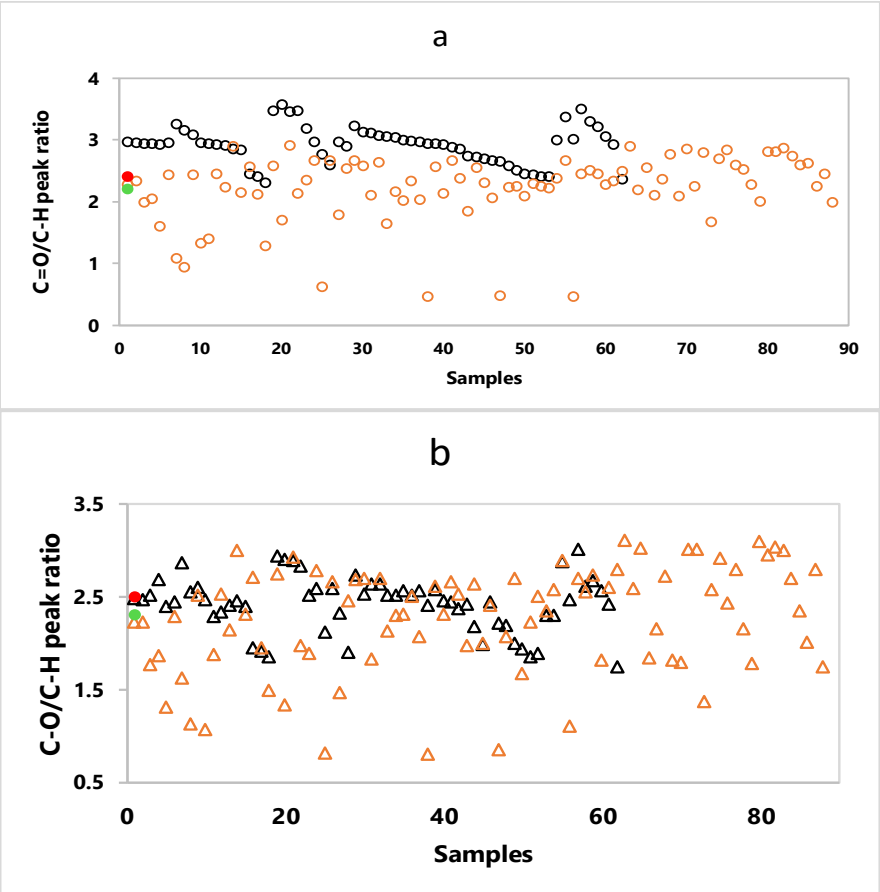


Figure 6.38 – C=O/C-H (a) and C-O/C-H (b) peak ratio on negatives with CAB (black) and CA (orange) supports, and CDA (green dot) and CTA (red dot) model films. Spectra normalized for C-O-C stretching (1051 cm^{-1}).

Two different conclusions may be drawn from the results presented in Fig. 6.38 (a,b), i) one pointing out for a clear separation between CAB and CA samples, indicating the possibly of a lower acetyl content for CA samples comparatively with CAB samples (Fig. 6.38,a), and ii) similar C-O/C-H ratios above 1.5 forbid distinctions between CA and CAB samples (Fig. 6.38,b). However, bellow 1.5 ratio a clear tendency is observed revealing that the lower ratios obtained are all attributed to samples with CA support (total of 11). The significative decrease of the C=O/C-H and C-O/C-H ratios determined for a set of eleven negatives with CA support indicate the extensive loss of acetyl groups (deacetylation). Additionally, such as presented in Fig. 6.36 (inset at right), for this set of negatives, spectral changes in the C-O-C stretching region (1051 cm^{-1}) indicate changes in the backbone of the polymer (chain-scission).

By correlating the C=O/C-H and C-O/C-H ratios with the O-H/C-H ratios it is possible to confirm the severe condition of this samples for which the decrease of the acetyl groups is correlated with an increase of the hydroxyl groups. Thus, significant spectral in peak ratios are correlated with samples condition. As the level of visual degradation increases an increase of the O-H/C-H ratio from 0.1 (minimum) to 5.7 (maximum) was obtained (Fig. 6.37). In agreement, the C=O/C-H and C-O/C-H ratios decrease, from 2.9 to 0.5 and

3.1 to 0.8, respectively (Fig. 6.38, a and b). Moreover, the degradation is also noticed by a shift of the O-H peak from 3396 to 3641 cm^{-1}. In the C=O region a peak shift from 1751 to 1724 cm^{-1} was observed. These results indicate the extension of the deacetylation of the films assessed and support the visual assessment results presented previously. Regarding plasticizers, in this study, it was not intended to perform an extensive identification and assessment of plasticizers. The common plasticizers used to improve CA's properties were dimethyl phthalate, diethyl phthalate and triphenyl phosphate (compounds alone or mixed), while for CAB polymer di-n-hexyl adipate and di(2-ethylhexyl) succinate were used (Fordyce and Meyer 1940; Hamrang 1994).

Concerning CAB polymer, its compatibility with highly water-resistant and non-volatile plasticizers was highlighted (Fordyce and Meyer 1940). Thus, comparatively with CA polymer, the plasticizers used to improve CAB polymer properties, are retained at higher concentrations and for prolonged periods of time. In part, the CAB-plasticizers system may be the main justification for the improved weathering characteristic of CAB polymer over CA polymer (Fordyce and Meyer 1940). In opposition, the plasticizers used in the production of CA's products have different behaviour. For instance, diethyl phthalate (as other phthalates) is gradually loss due to the excessive quantity used in the production, its vapour pressure or to the rate of diffusion (Fordyce and Meyer 1940). Thus, with ageing, it is expected that the diethyl phthalate degrades along with CA polymer decay (Williamson 1994). Moreover, since CA polymer tend to severely degrade when exposed to high relative humidity, the water solubility of plasticizers is of interest once the affinity of those with moisture may dictate their stability and contribution for the decay of CA polymer. From the three common plasticizers used in CA polymer, TPP has the lowest water solubility (0.002 %)[122], additionally, the volatility of the two phthalates was also highlighted (Richardson et al. 2014; Giachet et al. 2014). Possibly for those reasons, it was pointed out that under archival conditions, the rate of decay of TPP is lower than for the phthalates compounds (Williamson 1994). However, and as explained[123] ,TPP decay and its contribution for CTA degradation should not be forgotten (Shinagawa, Murayama, and Sakaiano 1992).

In sum, the properties of plasticizers contribute for the assorted degradation pathways found in photographic negatives with supports from CA family. Given the severe degradation found in samples with cellulose acetate support, it was found relevant to perform the identification of plasticizers within that samples. However, CA and plasticizers share many overlapping peaks, which hinder their identification. Thus, to confirm the type of plasticizer present in samples found in Severe condition, the film base and a crystalline plasticizer exudation found in the surface of one negative were analysed by Raman spectroscopy. In Figure 6.39, Raman spectra of CA model film (a), plasticizer (crystal) (b), and samples in severe and fair condition (c and d) are presented; the

[122] The water solubility of dimethyl and diethyl phthalate is 0.305 and 0.150, respectively (Fordyce and Meyer 1940).

[123] See section 2.5.3, page 64.

molecular fingerprints of cellulose acetate (blue) and TPP plasticizer (red) are highlighted. A strong peak at ~1000 cm^{-1} (benzene ring) as well as weak peaks at 1232 (C-O-C stretching vibration), 750 – 770 (C-O) 719 – 726 (C-O-P deformation) and 616 cm^{-1} are attributed to TPP plasticizer, while peaks at 1041 (C-O-C stretching vibration), 1601 (ring stretching) and 3075 (C-H stretching) are attributed to diethyl phthalate (Socrates 2004; Tsang et al. 2016).

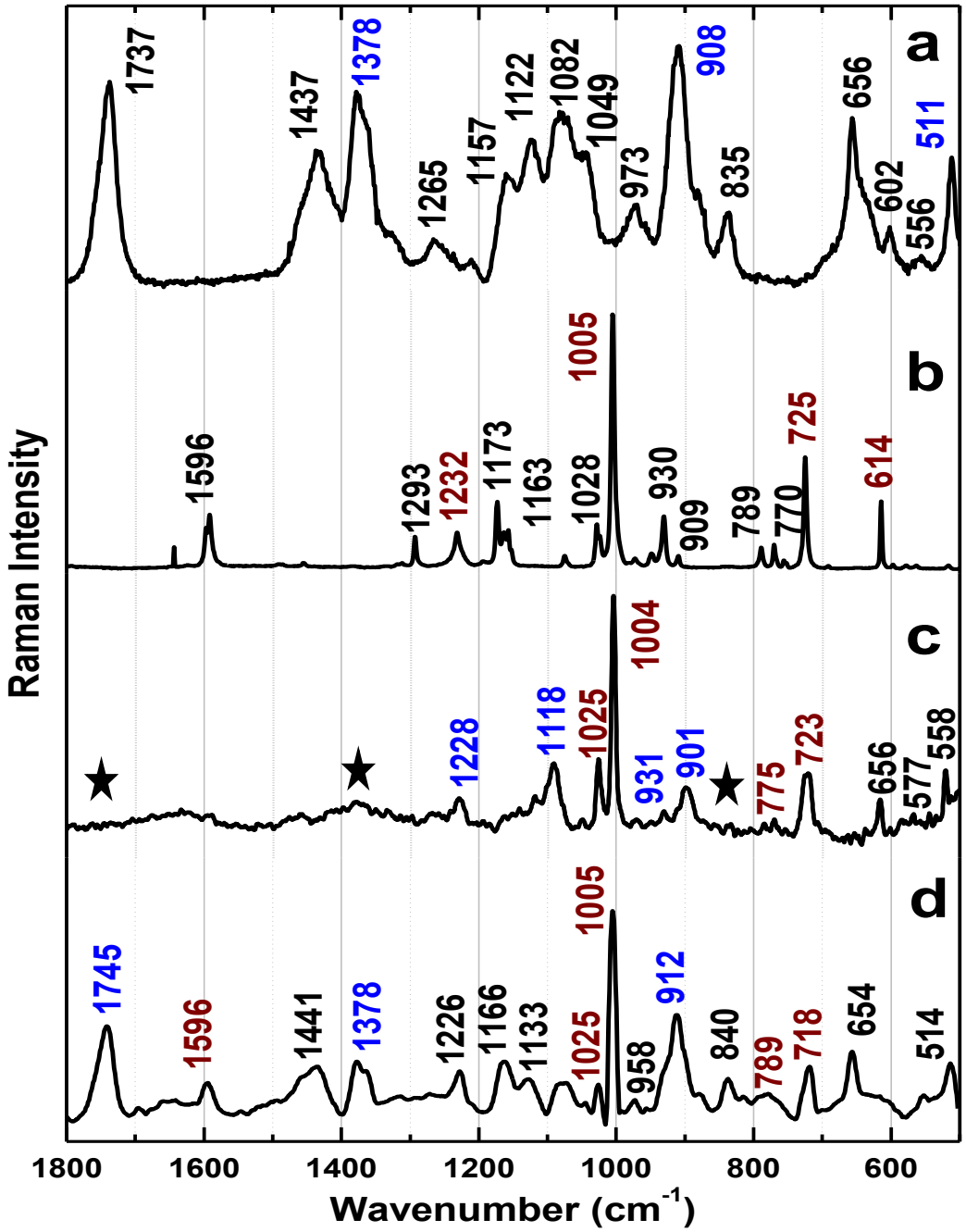


Figure 6.39 – Raman spectra of CA model film (a), TPP exudation (crystal) (b), CA film support from a sample in visible severe degradation (c), and sample in fair condition (d).

None of the peaks attributed to phthalates was identified. Moreover, the analysis of the crystal exudate from a severely degraded CA sample, TPP was identified (Fig. 6.39 b). A

careful observation of the four spectra presented in Fig. 6.39 (a to d), allow to conclude that, independently of the sample condition, TPP is present in the composition of the CA polymer (wavenumbers in red) being recorded a shift of the peaks along with the decrease (to total disappearance) of the intensity of the peak at 1596 cm^{-1}. This finding agrees with what was discussed above, indicating that while phthalate plasticizers may have volatilized, TPP is retained in the bulk or in surface of the polymer even if it is severely degraded. It is also important to mention that FTIR and Raman spectroscopy may lack the sensibility to detect traces of other plasticizers that might still being in the composition of CA polymer (Schilling et al. 2010).

Concerning cellulose acetate, the main peaks attributed to this polymer are identified (blue) in Fig. 6.39 (a). Raman peaks assignment for CA is presented in Appendix IV.

As is shown in Raman spectra, significative spectral changes are found mainly at ~1745 (C=O stretching vibration), ~1375 (C-O-C stretching vibration), ~840 cm^{-1} (C-H stretching vibration), which allow to assess the condition of the samples (Fig. 6.39, c and d). As highlighted in Fig. 6.39 (c, star) a complete loss of the intensity of the peaks in the aforementioned spectral regions indicate deacetylation (at ~1745 cm^{-1}) and changes on the backbone of the polymer (at ~1375 cm^{-1}).

In this study the plasticizers were not extracted and their contribution for the intensity of the peaks and assessment of the film support condition was assumed. Regarding the contribution of plasticizers for the composition and stability of the film supports, for samples with cellulose acetate butyrate and cellulose acetate support, plasticizer (1488 cm^{-1})/C-H peak ratio (absorption) in the FTIR spectra was calculated (Fig. 6.40). The selection of the peak at 1488 cm^{-1} relied on its presence on each sample from this set and due to its relative stability. By calculating the ratio, it was also intended to correlate the correspondent results obtained by pH and hardness measurements carried out in this study and understand if there was a correlation between those that might be reflect the chemical and physical decay of the samples examined.

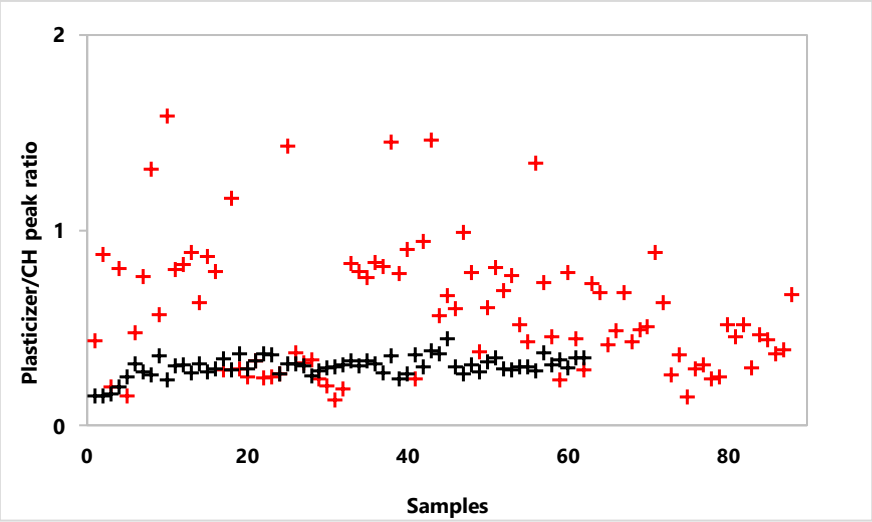


Figure 6.40 – Plasticizer (1488 cm^{-1})/C-H peak ratios (absorption intensities) results for cellulose acetate butyrate (black) and cellulose acetate-based (red) negatives from SP collection. Spectra normalized for C-O-C stretching (1051 cm^{-1}).

On cellulose acetate-based negatives, an increase of the ratio, from 0.3 to 1.6, was obtained, confirming that the plasticizer is retained in the bulk or in the surface of the film independently of the molecular changes ongoing on the polymer matrix. Based on μ-FTIR and Raman analysis, the ratio obtained is associated with the loss of intensity of both plasticizer and C-H linkages and reflecting the decay of the CA polymer. Again, this conclusion may only be addresses for the plasticizer identified, which is TPP. Regarding the results obtained for samples with a CAB support, the ratios varied between ~0.2 and ~0.5, confirming that, as previously discussed, for this polymer plasticizers are still retained in the bulk of the polymer. Comparatively with negatives with CA support, the results confirm that negatives with CAB support are in Good condition, according to the fact that this polymer is chemically and physically more stable.
With the aim to understand how the chemical and physical behaviours of these historical films could be assessed with simple, non-destructive and reliable techniques, pH and hardness measurements were performed.

pH measurements
Acidity is extensively related with cellulose ester films decay (Adelstein et al. 1992; Edge et al. 1989). It may also be correlated with the decay of plasticizers (Fordyce and Meyer 1940) however, since that hypothesis in beyond the focus of this study, the pH measurements carried out neglected such influence. Therefore, to assess the chemical decay of the samples, pH was measured assuming that the average measurements obtained will express the behaviour of the layers and compounds present in each sample.

In Fig. 6.41 the results obtained for samples with CAB and CA support are presented along with standard deviation (±SD). For negatives with CA support the average pH values obtained range between ~7 and ~3, while for negatives with CAB support it ranges between ~6 and ~5. These results agree with previous presented, indicating insignificant chemical changes for the set of negatives with CAB support. The estimated errors (standard deviation) for the pH measurements on the set of CAB negatives reflect the biological contamination (fungus) visually perceived on the surface of the negatives.

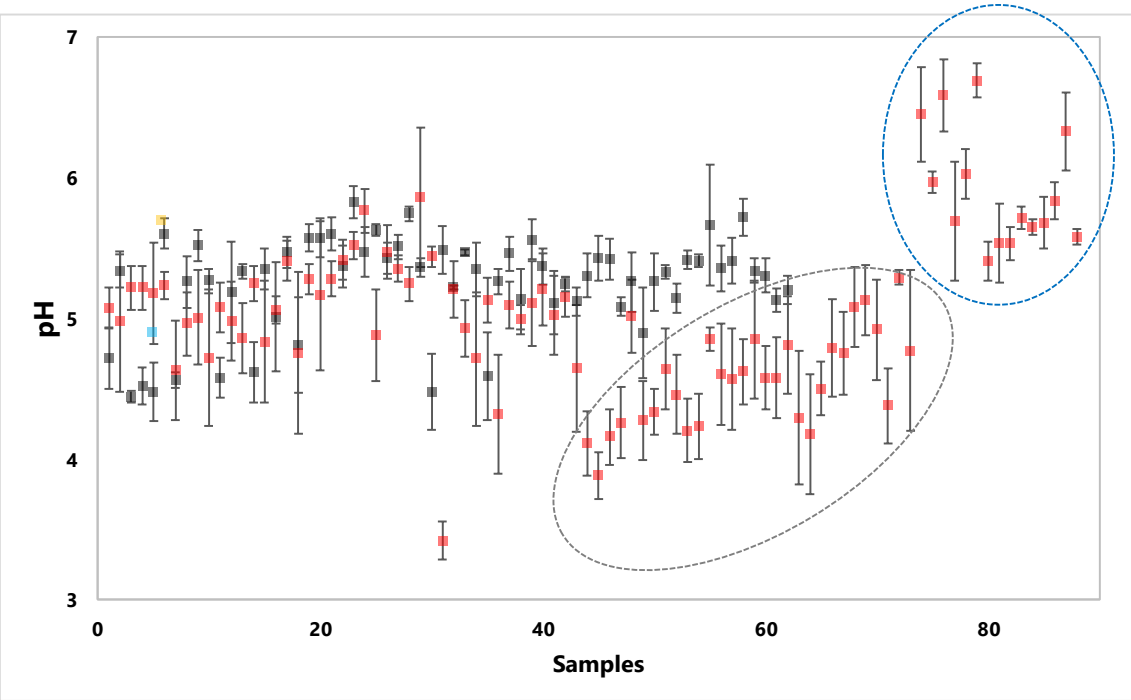


Figure 6.41 – pH average values ± SD obtained for negatives with CAB (black) and CA (red) supports from SP collection, and CDA (blue) and CTA (yellow) model films.

On cellulose acetate-based negatives a significative variance of the pH is noticed. A closer observation allowed to conclude that the highest pH values (~6 to 7) were obtained for samples with 60mm format (Fig. 6.41 a, blue circle). Additionally, it was also observed that the lowest average pH values obtained (~4 to 3) correspond to negatives with blue hues in the anti-halation layer (10 samples), plasticizer exudations (22 samples), heterogeneous decay visually perceived (3 samples), and corrective treatments of the image (1) (Fig. 6.42, a to d, respectively).

Figure 6.42 – Case studies with blue hues in the anti-halation layer (a), plasticizer exudations (b), heterogeneous decay visually perceived (c), and corrective treatments of the image (d), for which pH ~4 - 3 were measured. © DGPC-ADF/ Credit: Luisa Oliveira.

Moreover, it was also noticed that samples with extensive channelling have pH values equal or above 5, indicating that the acetic acid resulting from chemical decay was released. These results allow to conclude that in part the pH values obtained reflect the decay of cellulose acetate films. However, due to the contributions described (e.g. anti-halation dyes, plasticizers exudations on the surface of the films, heterogeneous decay and corrective treatments of the image) it was not possible to establish a pH marker based on which practical preservation decisions may be supported.

Concerning heterogeneous decay of the samples, it was found a set of three negatives in which there are severely degraded areas with plasticizers exudations, channelling and brittleness as well as areas completely flatten, showing only some signs of warping. For these cases different pH values were obtained according to severe (~5) or fair (~4) condition areas. One plausible cause for such heterogeneities may be the original storage method that, due to the lack of individual enclosures, favoured the contamination of the negatives which were in contact with each other inside boxes that, when opened an intense acetic acid odour was noticed. For one negative, the low pH value obtained is apparently related with corrective treatments of the image (Fig. 6.42, d). For the sake of clarity of the discussion of the finding's discussion in the study of SP collection, the identification of the compounds found in the image layer of this negative are presented at the end of this section. Again, the estimated errors (standard deviation) for the pH measurements reflect the contributions aforementioned.

However, excluding the negatives for which the aforementioned contributions were found, a careful correlation between average pH values and visual observation allowed to suggest that when visual signs of degradation start to be perceived, pH decrease to values of ~4. A correlation between low pH values and samples with blue anti-halation hues was established. For these samples the average pH values determined are equal or below 4. To this result is added the fact that these samples have the 'U' shape notch code. These results are highlighted with a grey circle in Fig. 6.41.

The pH measurements allowed to distinguished sets of samples, however the contributions found on the surface of the samples prevent the detection of a marker. Thus, avoiding such contributions, hardness measurements were carried out with the aim to assess the condition of the samples based on physical properties.

Hardness measurements

The average hardness results obtained for negatives with CAB and CA supports, and CAB and CTA model films are presented in Fig. 6.43.

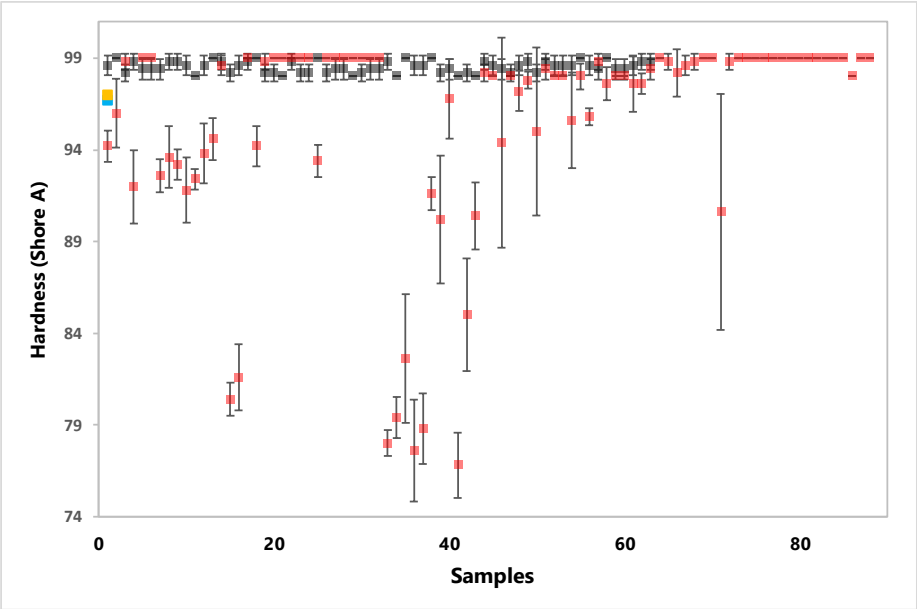


Figure 6.43 – Average hardness values and ± SD obtained for cellulose acetate butyrate (grey) and cellulose acetate-based (red) negatives from SP collection, and CDA (blue) and CTA (yellow) model films.

The average hardness values obtained for negatives with CAB support range between 99 and 98 (Fig.6.43, grey). On negatives with CA support, the highest hardness values (99 – 98 Shore A) were obtained for 65% of the negatives, and for the remaining films the hardness values lower until ~77 (Fig. 6.43, red). The consistency of the results obtained for negatives with CAB support suggests that those are in Good condition. Concerning samples with CA support, it was observed that as the level of visible degradation increases, there is a decrease in hardness. This finding is also supported by the increase of the O-H/C-H ratio and decrease of the C=O/C-H ratio, that allow to assess the formation of polar groups (O-H) and loss of acetyl groups, reflecting the hydrolysis of the CA support and consequent loss of physical properties. Thus, taking in consideration these results, with the aim to correlate the decrease of hardness with the deacetylation (and chain- scission) determined with C=O/C-H ratio, the Pearson correlation coefficient was determined for samples with CA support (which showed variations). For this case a positive correlation (0.4405) and a *p*-value of 0.00002 was obtained. This result allows to suggest that the analytical techniques used (IR spectroscopy and hardness measurements) allow to assess the condition (physical properties) of the negatives.

The average hardness values obtained for historical films were compared with those obtained for CDA and CTA model films (without plasticizers). As is possible to observe in Fig. 6.43, both model films have hardness values of ~97 Shore A. Comparatively, the historical films lacking visible degradation signs have hardness values above the ~97 Shore A. These results allow to suggest that hardness of the films may be related with plasticize and gelatine layer. As previously said, TPP is retained on the bulk or surface of the CA polymer. Thus, it is believed that the hardness values are dependent of the deacetylation and chain-scission reactions as well as from the plasticizer retained.

Therefore, the Pearson correlation was determined in order to understand if there is a correlation between hardness and loss of plasticizer. For this a negative correlation (-0.507203) and a *p*-value of 0.000 was obtained, indicating that despite of being detected on the bulk and surface of the samples, a decrease of the plasticizers has occurred being reflected on the hardness of the films.

Thus, based on the results obtained, it is suggested that by measuring hardness it is possible to assess the physical condition of negatives with CA support. Concerning the hardness value that marks the potential risk of increasing degradation, based on the data acquired, within the range of 99 to 98 Shore A negatives maintain their physical properties. Below that range, a decrease of hardness indicate that chemical changes are taking place in the CA polymer and consequently are reflected in the loss of physical properties. This might be the marker for decision making necessary for assess film decay and establishing priorities for conservation of historical collections. Additionally, closer observation of the hardness results allowed to confirm that, as for pH measurements, case studies with notch code with a 'U' shape (but not necessarily only with blue hues) have the lowest hardness values obtained.

μ-EDXRF results

The μ-EDXRF analysis was performed for identification of the chemical elements in the image of three samples from SP collection for which bluish and pink-reddish hues were perceived (Fig. 6.44).

Figure 6.44 – Negatives with bluish (left) and pink-reddish (centre and right) hues. Case studies SP 325 (left), SP 326 (centre).

μ- EDXRF spectra of the three samples analysed are presented in Fig. 6.45.

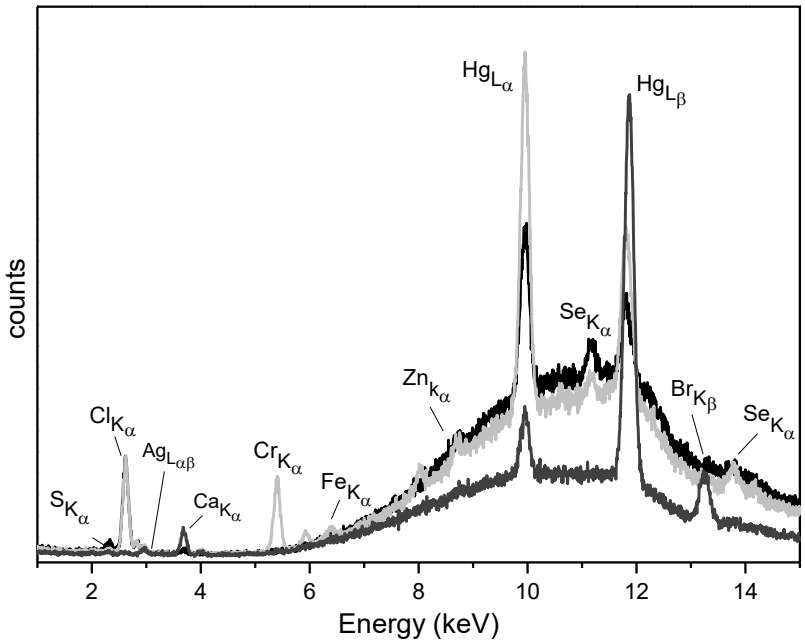


Figure 6.45 - Micro-EDXRF spectra of the negatives SP 325 (black), SP 326 (light grey) and SP 716 (dark grey) showing bluish and pink-reddish hues.

The main elements identified for negatives SP 325 and SP 326 are mercury (Hg), chlorine (Cl) and selenium (Se). Despite the similarity of hues between the negatives SP 326 and SP 716, the results of micro-EDXRF confirm that there are different elements in the image. The presence of Hg is common to the three negatives; however, SP 716 spectrum reveal the presence of bromide (Br) (Fig. 6.45, dark grey). On sample SP 326, additional peaks for chromium (Cr) and iron (Fe) were identified. Additionally, based on micro-EDXRF results and visual observation is possible to conclude that the photographer performed two types of actions on the image: a general and a local treatment. The negatives SP 326 and SP 716 were submitted to a general treatment resulting in a general pink-reddish tonality while negative SP 325, regardless the overall bluish colour, was locally treated as it is possible to confirm by the pink-reddish hue on the face and shirt of the man (Fig. 6.45).

Based on the results achieved it is suggested that SP 325 and 326 have been submitted to a s*ubtractive reduction* treatment *with a* mercury and cyanide (Eder's solution) solution and selenium toning. For negative SP 316 it is suggested that a *superproportional intensification* treatment was carried out with a mercuric bromide bleach; sodium sulfite redeveloper solution.

By crossing µ-FTIR , Micro-EDXRF and pH results obtained for negative with index ref. SP 325, it was found that in this case the pH (previously discussed as a contribution of corrective treatments for lowering pH) is dependent of the decay of the film support, for which a decrease of the intensity of the peaks at C=O and C-O was observed.

6.3.4 Molecular assessment of Silva Nogueira collection

In the set of samples from SN collection, by μ-FTIR analysis two types of supports were identified: CA (11 specimens) and CAB (11 specimens). Ratio determinations followed those presented in the previous section. In Fig. 6.46 (a,b), the O-H/C-H and C=O/C- H peak ratio (absorption) per sample are presented.

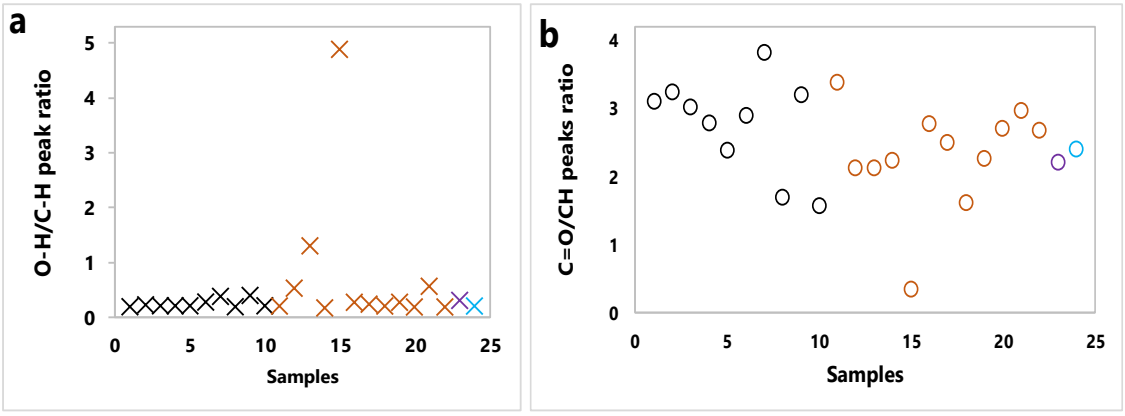


Figure 6.46 – O-H/C-H (a) and C=O/C-H (b) peak ratios (absorption intensities) results for cellulose acetate butyrate (black) and cellulose acetate-based (orange) negatives from SN collection, and CDA (violet) and CTA (blue) model films (without plasticizers and gelatine layer).

Data allow to conclude that beside two case studies (SN 809 and SN 816), no significant differences are found in the O-H/C-H peak ratios. Moreover, the ratios determined for C=O against C-H allow to observe minor differences between samples, except for one sample (SN 816) for which a decrease of the acetyl groups indicates deacetylation. By comparing the results obtained for historical films analysed with the results for CDA and CTA model films (violet and blue, respectively), it is possible to suggest that beside case study SN 816, the differences on the ratios determined are not significant but show different molecular conditions of the film supports that may be acknowledged by the values of C=O/C-H peak ratios (absorption) determined (Fig. 6.46 a,b). According to these results, beside the specimen SP 816, the loss of acetyl groups is not simultaneously followed by an increase of hydroxyl groups. Figure 6.47 depict the spectral changes correlated with the deterioration of cellulose acetate-based films.

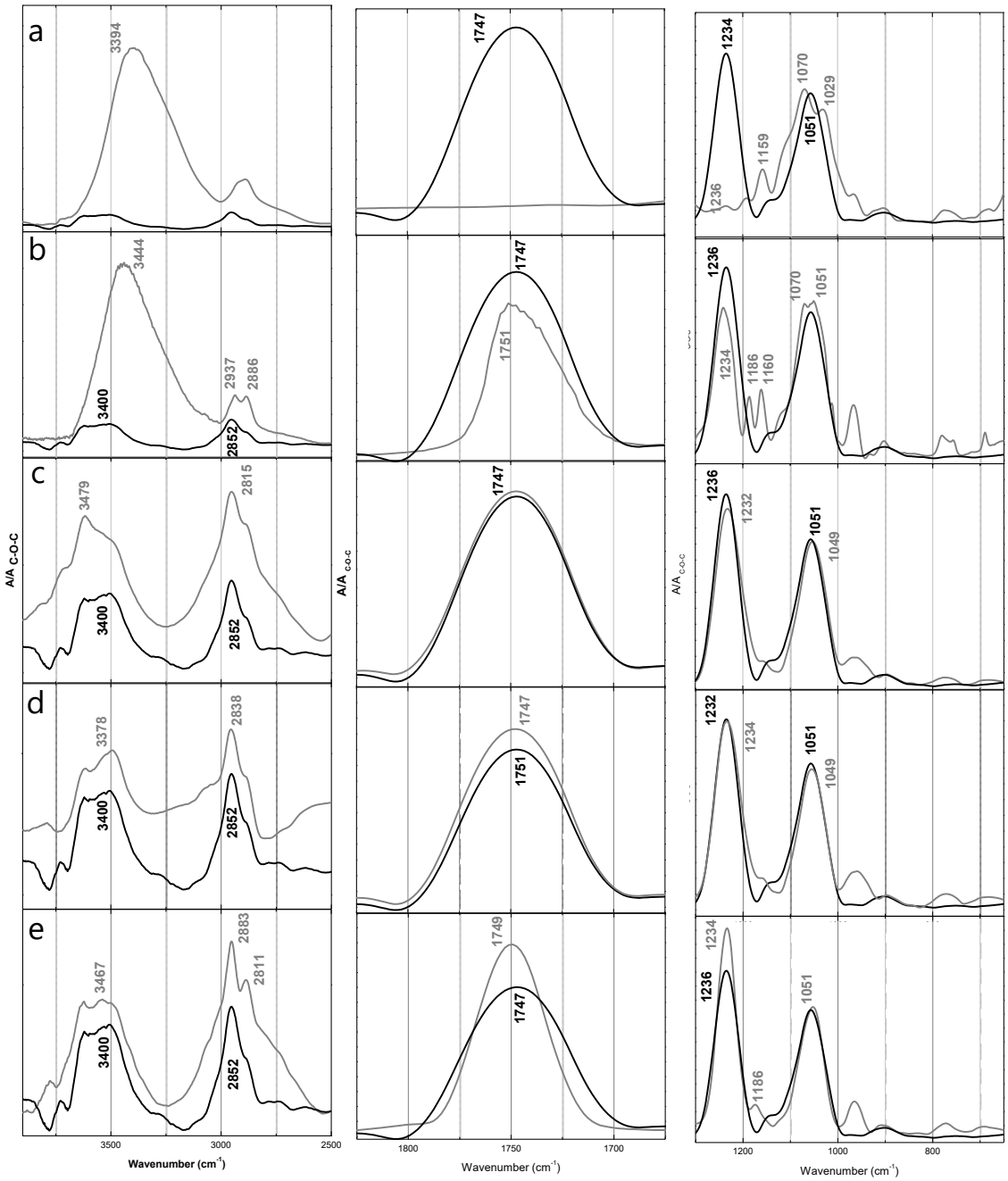


Figure 6.47 – Infrared spectra of a CA model film (black) and cellulose acetate-based negatives from SN collection (grey) showing different condition grades: O-H and C-H stretching region (left), C=O stretching region (centre), and C-O-C stretching region (right). Good condition (2): SN 1121 (e). Fair condition (3): SN 864 and 855 (d,c). Poor condition (4): SN 809 (b). Severe condition (5): SN 816 (a).

According to Fig. 6.47, from CA model film (black) and negatives with CA support with different conditions (Fig. 6.46 a to e, grey) several spectra changes are observed in O-H, C-H, C=O and C-O-C stretching regions. The first clear change is the shift, broadening and increase of the intensity of the O-H stretching absorptions at ~3400 cm^{-1} (Fig. 6.47 a-e, left) attributed to the increasing formation of hydroxyl groups that result from the

chemical decay of CA polymer. Along with this change, the decrease of the C=O and C-O stretching absorptions at ~1750 cm^{-1} and ~1236 cm^{-1} are also observed (Fig. 6.47, grey, centre and left). Particularly for the case study in condition 5 (Fig. 6.47a), in the C-O-C stretching region significant spectral changes are observed indicating changes on the polymeric chain (chain-scission) and return to the cellulose structure. This finding, pointing out the occurrence of deacetylation and chain-scission, agrees with the literature (Edge et al. 1989; Littlejohn et al. 2013; Giachet et al. 2014). On negatives with CAB support, regarding the ratios determined, by comparison with negatives with CA support, insignificant spectral changes were observed. In Fig. 6.48 the FTIR spectra of cellulose acetate butyrate-based negatives from SP collection (Good condition, 2 specimens, blue and black) and SN collection (Fair condition, one specimen, grey) are presented.

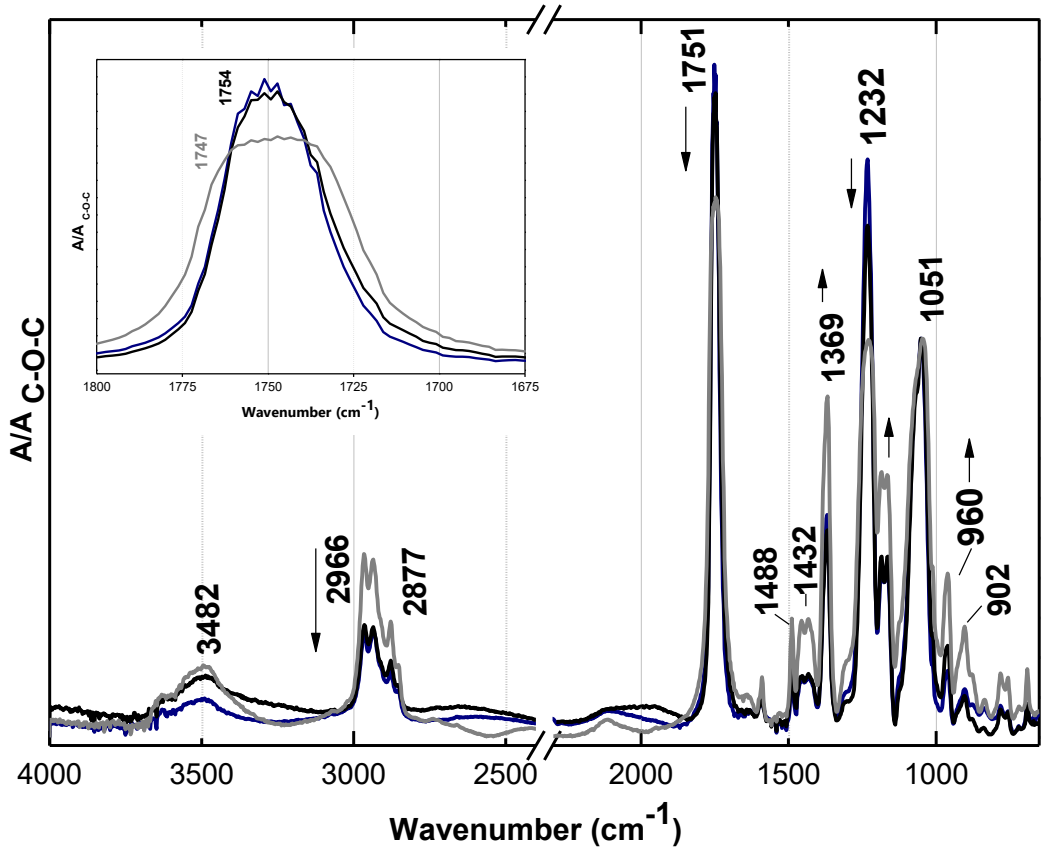


Fig. 6.48 – FTIR spectra of cellulose acetate butyrate-based negatives from SN collection showing different condition grades. Good (2) condition: SP 98 and SP 100 (blue and black). Poor (4) condition: SN 834 (grey). Inset: detail of the C=O region from 1800 to 1675 cm^{-1}. Spectra normalized for C-O-C stretching (1051 cm^{-1}).

By comparing the FTIR spectra of the three specimens it was possible to confirm that, overall, minor spectral changes were observed (Fig. 6.48). These spectral changes occur mostly in the C=O (~1750 cm^{-1}) and C-O (1232 cm^{-1}) stretching regions, which indicate deacetylation (Fig. 6.48). On sample in Fair condition (Fig. 6.48 grey), along with the

decrease of the absorption intensities the regions attributed to acetyl groups (~1750 and 1232 cm^{-1}) was observed. Additionally, an increase of the absorption intensities between 3000 and 2840 cm^{-1} (νCH_2 and CH_3), and at ~ 1432 cm^{-1} and ~1369 cm^{-1} (C-H bending regions) are detected. However, comparatively, in O-H stretching region, insignificant spectral changes are observed. Thus, it is suggested that the sample in Fair condition is at the initial stage of deacetylation, supporting the visual assessment performed.

Regarding pH and hardness values, a significant variance was obtained. Figure 6.49 depict the average pH and hardness (Shore A) values and SD obtained for negatives with CAB and CA supports, from SN collection as well as for CDA and CTA model films.

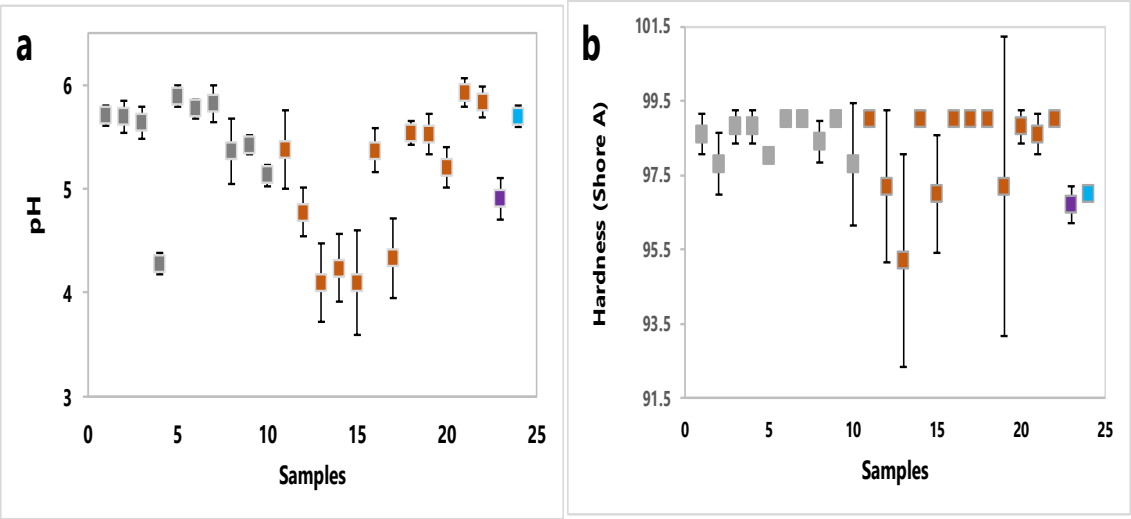


Figure 6.49 – Cellulose acetate butyrate (grey symbol) and cellulose acetate-based negatives (orange symbol) from SN collection (total of 22) and CDA (violet) and CTA model (blue) films: pH (a) and hardness (Shore A) (b) average values and ± SD.

Overall, on negatives with CAB support (grey symbols), apart from the case study SP 903 (with the lowest pH value in the set of specimens with CAB support) minor differences on pH and hardness values were obtained. However, on negatives with CA support, pH and hardness values varied significantly. The results obtained agree with the spectral changes observed. Thus, it was concluded that both, pH and hardness measurements, reflect the chemical and physical properties of the historical films examined. Regarding the standard deviation, the results reflect the heterogeneities (chemical and physical) found on historical films. Examples of the heterogeneities found are presented in Fig. 6.50, where uneven discoloration (on both negatives) and warping are visible. A careful observation allowed to conclude that there is a correlation between discoloration (hues) and pH measurements (for intense yellowing, lower pH values were obtained). Moreover, extreme distortion was observed for specimens in Poor and Severe condition. In these cases, the hardness measurements varied significantly from the edge (lowest values) to

the centre of the objects[124]. These results are identical for case studies with cellulose acetate and cellulose acetate butyrate supports from SP collection.

Figure 6.50 – Cellulose acetate-based negatives from SN collection showing discoloration and distortion/warping. © DGPC-ADF/ Credit: Luisa Oliveira.

Again, as for samples from SP collection, by correlating μ-FTIR, pH and hardness result it is possible to conclude that, comparatively with samples with CAB support, negatives with CA support show extensive degradation.

Additionally, it was also confirmed that specimens with a notch code with a 'U' shape are more degraded (lowest C=O/C-H peak ratio, and lowest average pH and hardness values). However, in this set, there are no films presenting blue hue. This finding allowed to confirm that, despite the anti-halation dye used, historical films with the 'U' shape notch code tend to degrade more than other samples examined in this study. Considering the historical references to CAB polymer that describe it as an improved product with superior chemical and physical properties and high dimensional stability (Malm and Hiatt 1954; Malm, 1942; Calhoun as cited in Horvath 1987), the results obtained confirm those references. However, by correlating the Infrared spectroscopy identification and assessment with the notch codes found in the collections, a straightforward identification of the film supports was design that in the near future can support caretakers on the identification and assessment of film collections.

[124] Detailed information about data collected per case study may be consulted in the database designed in the framework of this study.

6.4 Near -infrared spectroscopy: attempts for fast and accurate identification of film-based negatives

The results accomplished with the questionnaire and macro and molecular assessment reflect the necessity of developing new methodologies for identification and assessment of film-based negatives. FTIR and Raman spectroscopy allowed to perform the accurate identification and characterization of the negatives. However, both techniques demand sampling (are destructive), requires sample preparation and, at the end, considering large collections, are time consuming. To overcome these drawbacks, the negatives were analysed by Fourier-Transform Near-Infrared (FTNIR) spectroscopy. Due to the fundamental nature of NIR spectroscopy (with weak and overlapping absorptions), and due to the absence of a NIR spectral database, the primary results obtained wit FTIR and Raman spectroscopy were useful for understanding the NIR signals and eventually perform the complete NIR band assignment.

First tests revealed that spectra performed in dark areas of the image, where silver halides are present, showed higher noise and bands with lower resolution. Taking that in consideration, four independent analysis per sample were performed, all on the transparent edges of the negative. In Fig. 6.51, Near-infrared spectra of negatives with CN, CAB and CA supports are presented.

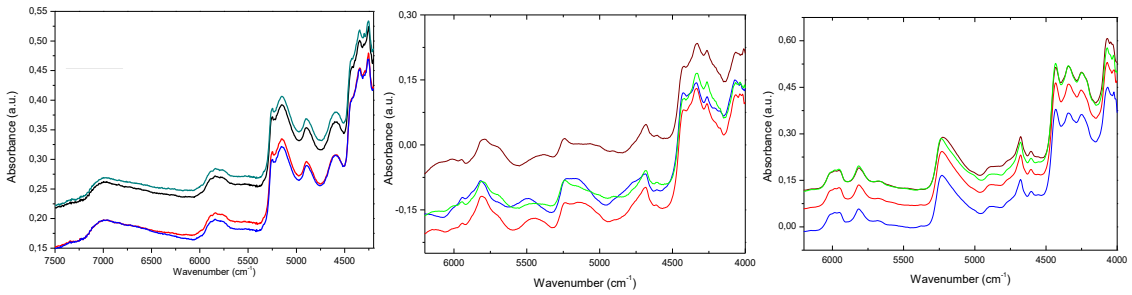


Figure 6.51 – Near-infrared spectra of negatives with CN (left), CAB (centre) and CA (right) supports.

A closer observation was given for the first overtone region (~7000 to ~5000 cm^{-1}) and combination bands region (~5000 to 4000 cm^{-1}), where noticeable absorption bands related with overtones and combinations bands attributed to molecular vibrations of -CH, -NH, -OH functional groups are observed (Socrates 2004). Significative spectral changes are observed however the attribution to specific material or condition was difficult to obtain due to the contributions of gelatine layer, anti-halation dyes regenerated and chemical corrective treatments. Additionally, thickness and scratches on the surface of the surface of the negatives also led to high noise and loss of resolution of the bands. Even by extracting analytical information from such broad and overlapping bands that reflect physical and chemical properties with statistical methods (e.g. chemometrics) it was concluded that due to the large variables found in this type of materials another approach must be designed. The work performed in this study will

serve for that purpose, since a large set of samples, is already characterized and it will be usefull for the development of calibration methods.
Despite of the inconclusive results, in was confirmed that this analytical technique allows to perform fast and non-destructive analysis of the films and, by investing in more research, it is believed in a near future this method can replace micro-destructive tests and will contribute for the preservation of film collections.

6.5 Conclusions

The collections selected showed how challenging cellulose nitrate and cellulose acetate-based negatives are. Overall, the survey and analysis carried out in this study allowed to get an insightful knowledge of the photographic materials used by Portuguese photographers from the 1930's to 1950's, and simultaneously to assess the condition of the collections studied. For that a large set of negatives was selected and examined.

By studying the ECC collection it was intended to acknowledge the photographic work performed by Portuguese photographers that have worked in African countries occupied by Portugal during the first half of the 20th century. The results obtained allowed to conclude that the negatives selected are in Good to Fair condition. Given the historical documentation and the photographer report, the storage conditions may have contributed for the preservation condition of the negatives.
The primary sources were also important for a first assessment of the hues visually perceived on the image layer. The purchase's invoices of mercury and iodine indicate the possibility of corrective treatments might have been performed. SEM-EDS and µ-EDXRF analysis results support this hypothesis, and additionally it allowed identifying other chemical elements, such as Cr and Fe. These two chemical compounds were indicated for temporary gelatine hardening, specially recommended as a prior treatment that could stabilize the gelatine before photographic processing. This recommendation was given to photographers that were working in the African countries, as a preventive measure for safeguard of the image layer. Regarding the presence of Zn, the storage system or cleaning solutions are suggested as plausible causes. The description of the storage system given by Cunha e Costa supported suggesting that the presence of Zn, as well as Ca, might result from the storage system. Furthermore, publications of that time reinforced the idea of the use of such storage system again to prevent the development of mold and detrimental effects of high relative humidity in the photographic negatives.

It also became clear that the photographer performed different types of corrective treatments of the image, launching new perspectives about the practice of colonial photography. By µ-EDXRF analysis of the image layer chemical elements on the image were identified. Based in these findings and visual observation a correlation between colours and chemical elements/corrective solutions was made. In this way, a valuable

contribution to visual recognition and understanding of the corrective treatments performed by Cunha e Costa was accomplished, that may also support the identification of such hues in other collections. A closer observation of the μ-EDXRF and pH measurements allow suggesting that there is a correlation between pH and type of corrective treatment. Thus, considering the correlation between low pH and Cr found, new preservation priorities may be launched since this chemical element has a detrimental effect on polymers. Additionally, the SEM-EDS results confirmed the presence of the transition metals identified by μ-EDXRF localized in the emulsion layer.

In primary sources, references to the purchase of Agfa film by Cunha e Costa was found. This information allowed answered the question about the type of photographic materials used, since the negatives lack brand references (lack edge printing). By encountering a single case study in which a notch code and internal reference to 'Kodak' (notchs are rarely found in case studies with 60mm format), the origin of the negative was questioned. Based on μ-FTIR analysis results, it was possible to suggest that Cunha e Costa used i) roll films from different brands or ii) in the same timeline of film production brands were producing films with different plasticizers formulations. This suggestion is based on the identification of additional peaks attributed to phthalate and phosphate families found in four case studies.

By analysing such a large set of film-based negatives it was possible to collect and correlate a wide range of FTIR spectra and pH average measurements. However, and unexpectedly, these results are not linear and have not shown a straightforward correlation between the absorption intensities ratios and pH, and consequently between VA and MA. Moreover, these results corroborate the reports on the difficulty to assess and determine a shift moment for cellulose nitrate film-based negatives' conservation condition.

In sum, despite of the macro and molecular changes observed, overall the case studies from ECC collection are well preserved. The results accomplished in this study show the wide range of variables found on these films, which difficulted establishing a relationship between VA and MA. Nevertheless, taking consideration the results obtained, the working methods and storage system described by Cunha e Costa might have promoted the stability and exceptional preservation of the ECC collection.

The study of the DGEMN collection allowed to assess nitrate-based negatives with distinct brands, assorted formats and different preservation condition attributed according to VA evaluation. Based on in μ-FTIR results it was possible to confirm that all case studies select have a nitrate support, and from that point it was possible to correlate this data with the notch code found in the set of case studies with large format. In this way a step for straightforward identification was accomplished. These results are relevant when considering that, three of the notch codes found have no additional information beside the notches and show different shapes associated with cellulose nitrate supports.

Moreover, in opposition to the 'V' code commonly attributed to cellulose nitrate film supports, 'U' and 'square' shapes were also identified as being used for this type of support (see Fig.6.14 g,h and i). Thus, it is expected that these results may support a first level identification and contribute for the daily work of caretakers responsible for film-based negatives collections. Additionally, these results contribute for the survey of a notch (broad 'U' shape) regarded in the literature by acknowledging to Ferrania brand (Fig. 6.14h). However, for small and medium formats, the results accomplished do not allow to contribute for a straightforward identification.

In what concerns the processing solutions and developing procedures undertaken by the photographers, the lack of information difficult the interpretation of some signs of degradation visually perceived. However, a careful survey allowed to conclude that improper enclosures and inadequate storage conditions (high relative humidity) might have influenced the preservation condition of the case studies. The overall pink and yellow discolorations observed were on the anti-curl layer and base, indicating the chemical decay of the negatives.

The μ-FTIR analysis enabled to confirm that all negatives have a cellulose nitrate base and led to the identification of assorted plasticizers' (camphor, TPP and phosphates) formulations in the negatives. From the total case studies sets established, by comparing FTIR peak ratios of all case studies analysed, case study fD 17602 have shown the lowest ratios, meaning the highest denitration observed. Despite the VA and MA correlation found, the μ-FTIR and pH and hardness results show no correlation. However, for nitrate-based negatives with 35mm format a pH 6 was consistently obtained.

Regarding the overall cellulose nitrate film-based negatives examined, by analysing the case study from MN collection new perspectives on the chemical degradation of nitrate-based negatives was developed in this study. The results point out for different degradation behaviours according to films thickness. Independently of the peak ratios determined, it was concluded that thicker films suffer from severe degradation (loss of chemical and physical properties), while thinner films tend to maintain their physical properties. The artificial ageing carried out confirm this finding. The reasons for such behaviour were not clarified, however, it has been reported by conservators that in their daily practice observed similar situations. This behaviour might be cause by the degradation products that are retained in the bulk of polymer of thicker films, while in thinner films those products are released. Future investigations should focus this issue.

In respect to cellulose acetate-based negatives, similar behaviour was observed, showing that comparatively, negatives with thicker supports severely degrade while negatives with thinner base are in preservation conditions ranging from Very Good to Fair. In part the condition of the negatives with 60 mm format may result from the CTA base, that in this study was not possible to accurately identify as so. About this issue, more analysis

should be done to confirm if this is a CTA base or if effectively thickness is the answer for the stability of negatives with medium format.
Moreover, the results confirmed the presence of negatives with CAB supports, which comparatively with cellulose acetate-based negatives with large format (9x12 to 18x24 cm) showed to be well preserved.
One of the main findings of this study is the identification of a set of negatives with cellulose acetate support, 'U' notch code and blue and brown hues that, consistently, showed severe degradation. This finding is particularly important considering the definition of priorities in a collection, since those may be easily identified and consequently removed from the collection without putting at risk other negatives.

Concerning pH and hardness measurements, the results proved that both methods allow to assess the condition of film-based negatives. The attempts performed with Near-IR analysis shown the potential of this analytical technique for the identification and assessment of film-based negatives. However, the sensitivity on which this technique rely demands more work to develop calibration methods.

Regarding the identification of plasticizers, Raman spectroscopy gave insightful information about the presence of the plasticizer allowing to confirm the suggestions proposed based on IR spectra. This information was important to understand the chemical and physical behaviour of cellulose acetate negatives. Moreover, Raman spectroscopy proved to be an important technique for the assessment of cellulose nitrate negatives by allowing to detect minor spectral changes that with IR spectroscopy was not possible to observe.

Aiming at contributing for the identification of films supports, a large set of notch codes was surveyed. A correlation between notch codes and type of film supports (identified by μ-FTIR analysis) is presented as well as contributions for the preservation of film collections (Fig. 6.52).

Except for CAB films, it was not established a sequence, a chronology or a specific order for disclosure the notch codes surveyed, it was only considered the film type. For the display of notches in CAB films it was established a sequence according to machine number (number embossed close to the cuts). In the following diagram the notch codes identified are presented according to film support. In the diagram, highlighted with a red box, notch codes with a 'U' shape associated with a clear tendency for CA decay are presented.
These results confirm that 'V' shape was commonly used for negatives with a CN support, Comparatively, for CA a variety of notch codes was used. However, the notches used for CAB are more restricted in shapes, being the 'square' shape the most common. As is possible to see, in some cases, associated with notch codes comes a machine number that serve to indicate the film batch or quality inspector. Additionally, there are notch codes combined, 'V' and broad 'U 'or with 'wide divot' found for CAB films.

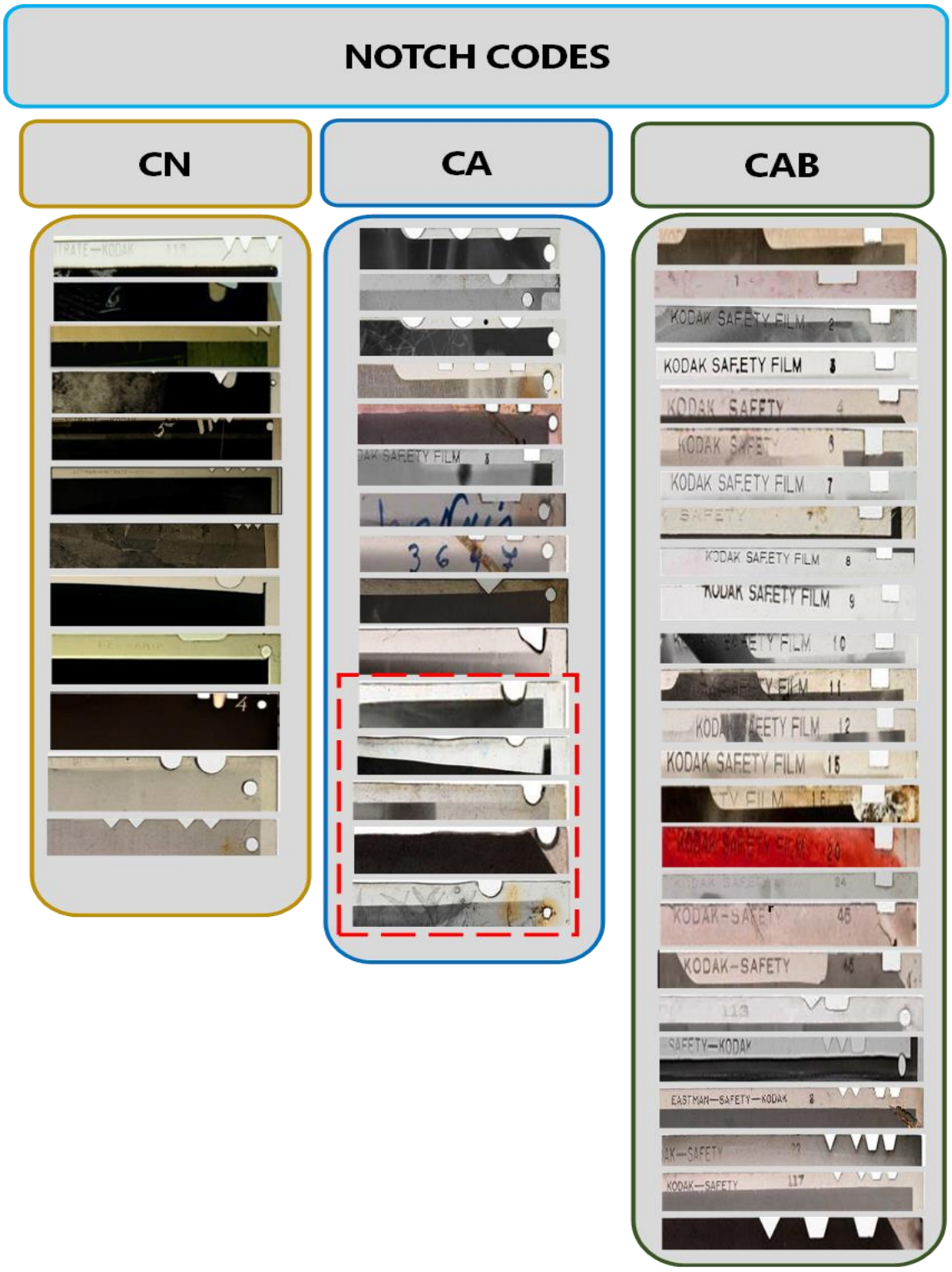


Figure 6.52 – Survey of notch codes found in the collections scoped, along with film support identification: CN at left, CA at centre and CAB at right.

Contributions for the preservation of film-based negatives

It is believed that the results accomplished in this study will improve the straightforward identification and assessment of film-based negatives. The correlation established between molecular identification of film supports and notch codes allows caretakers to perform an immediate identification of the films based on the marks identified in this works.

Based on the results obtained it is possible to establish priorities for the safeguard and preservation of the collections. Due to the high flammability of cellulose nitrate-based materials, these types of films will always have a high priority in film collections.

Secondly, the results have shown that large format or sheet films with CN and CA support tend to degrade severy and therefore should be considered a prioraty since the fast decay of those may contaminate and promote the decay of the remaining photographs in the storage room. These sheet film negatives should be monitored frequently.

Within the class of CA-based negatives, sheet films with a 'U' shape notch code with blue and brown hues in the anti-halation layer (overall or as a stain) (Fig. 6.52, red box) should be established as priority and removed for the collection. These negatives should, if possible, be store in a cool storage.

Regarding CAB films, identification and assessment are mandatory. However, according to the results obtained, these films may not be established as a priority in a preservation strategy. The list of notch codes provided in this work (Fig. 6.52) allow caretakers to perform a straightforward identification of CAB films.

Regarding the assessment, pH and, mostly, hardness (Shore A) have shown to be efficient tools for assessment of the preservation condition of negatives. The measurement of harness (Shore A) shown to be a new, non-destructive, low cost and easy to use method that may used by all caretakers. As previously presented in this work, hardness values below 98 Shore A should be considered indicative of chemical and physical decay of the film support, highlighting the necessity of separate those negatives from the remaining collection.

All the results obtained were used to develop a data-base on which caretakers may find data collected and use it for identification and assessment of the film-based negatives held in their institutions.

Chapter 7 - Concluding remarks and future perspectives

Chapter 7 - Concluding remarks and future perspectives

Cellulose nitrate and cellulose acetate film-based negatives are regarded for their ephemeral nature. In part, the instability of these materials is inherently associated with the fact of being the *oldest* plastics, thus, representing a broad experimental period in which assorted formulations were used to produce them. Therefore, the decay of cellulose ester film-based negatives may assume heterogeneous and complex pathways, challenging scientists, conservators and caretakers responsible for film collections to improve the preservation strategies currently used. Additionally, given the large amount of negatives and assorted intrinsic factors in which their permanence rely, the preservation of film collections demands continuous efforts on the development of innovative preservation strategies and implementation of environmental conditions that will extent the life span of the negatives and collections.
Beside these issues, it also became clear that over time efforst were made to develop field tests for that a broad type of caretakers coul assume the responsibility of performing some preservation tasks, e.g. identification and assessment. However, as already said despite the similarities shared by paper, books and photographic materials, the diverse typologies, compositions and nature of cellulose ester films demand an in-depth knowledge to understand their specificities and unique nature. Moreover, the handling of field tests relies on the existence of a budget that covers testing materials as well as hiring properly trained conservation staff to install and evaluate the end results.
The lack of conservation staff to ensure the preservation of enormous quantities of film-based negatives is one of the issues that cultural institutions must face.

The literature review allowed to understand that the majority of the knowledge about production methods and chronology reflect mostly the history of the North American companies that produced CN and CA film-based negatives. Additionally, it was also concluded that the preservation guidelines commonly used by caretakers are the result of investigations carried out mostly in the United States of America. In this study a gap on the chronology of production of film-based negatives in Europe was found. The interviews carried out in this study and the documentation found in AGFA-GEVAERT archive allowed to contribute for the definition of a chronology of the production of cellulose ester film-based negatives made in Europe. Additionally, issues concerning the production methods used were also launched, alerting for the risks of supporting the identification of the negatives on dating information.

Given the international panorama presented in, it was questioned "What is the scope of plastic negatives' collections in Portugal? And what is being made to preserve film collections in Portugal?" To access this information an online questionnaire was conducted. The results obtained were presented in Chapter 4. In this chapter notes on the commercialization and use of plastic negatives in Portugal was presented to place the selected collections in context for this study. Then, the results achived with the

questionnaire were given to support the importance of this work, being showed that there are huge quantities of plastic negatives with cellulose ester base in Portuguese collections. Moreover, it also revealed that besides Kodak, there is also a significant number of negatives produced by European producers, emphasizing the need of a broader knowledge about European film production.

The results also showed that the density test is commonly used for identifying film supports and odour is used to assess the condition of the negatives. Therefore, the results indicate that to perform identification and assessment tasks, Portuguese caretakers are continuously exposed to health hazards. These results support the priority of this study and the importance of developing new methodologies for the identification and assessment of film-based negatives.

Based on the critical review of the literature, the overview of methods currently used for assessment of films and with the results obtained with the questionnaire carried out, the methodology for this study was established. Besides the simple methods indicated in the literature review (edge printing, notch codes and macro assessment), analytical methods were selected to perform the accurate identification and molecular assessment of the negatives (Chapter 5).

Concerning the survey and macro assessment of the collections, important findings were accomplished. For start, by surveying these collections it was possible to, for the first time, identify assorted types of films, brands and notch codes present within Portuguese collections. Some of the brands and notch codes surveyed correspond to those presented in Appendix II. Additionally, it was possible to gather in-depth knowledge about the photographers working methods and associate the type of films used by each one of them. As expected, Cunha e Costa selected a medium format for his documentary photography work. Regarding the two portraitist, San Payo and Silva Nogueira, both used mostly sheet film, commonly from Kodak and an 'Unknown' producer. Moreover, it was concluded that the former used mostly negatives with 9x12 cm^2, and the later used larger formats.

An important contribution was given with this work by surveying a wide variety of notch codes. Most notches with 'V', 'square', 'wide divot' shapes were commonly used by Kodak. Many negatives with 'U' were identified, but lacking edge printing references that can support the identification of the producer.

Considering the preservation condition of the negatives selected, visually, it was concluded that negatives with small and medium format are well preserved, comparatively with sheet films. Additionally, about cellulose nitrate-based negatives, the lack of negatives showing extensive degradation led to the need to include a set of negatives from MN collection that could represent the typical decay of CN films described in the literature. The lack of cellulose nitrate-based negatives showing signs of

severe degradation was one of the first supprising findings of this work, supporting the reports given by other researchers.

The macro assessment also allowed to establish a first relationship between cellulose acetate-based negatives with 'U' shaped notch codes and a cleare tendency to severe degradation. This notch had been attbuted to Agfa/Ansco. Considering this information, it was suggested that these negatives may be examples of the the CDA products commercialized by Agda until 1955. Moreover, the insightfull information collected in the Agfa-Gevaert archive also supports the possibility of these negatives being *Cellit* products described in Chapter 3.

Considering the working methods of the photographers, the survey of ECC and SP collections allowed to detect negatives with different hues (pink, intense yellow, greenish, bluish, reddish, brownish and orange) visually perceived in the image layer. Therefore, these hues were associated with corrective treatments of the image performed by the photographers to improve the quality of the image. Concerning the ECC collection the extensive presence of these hues indicates a characteristical working methodology of the photographer. Regarding ECC collection, the historical documentation and the photographer report were crucial to understanding his working methods. By examining the image layer of a set of negatives with micro-EDXRF and SEM-EDS it was possible to identify the chemical compounds present on the image and correlate them with possible intensification and reduction solutions used to improve the image density. This finding brought insightful knowledge about the image improvement treatments carried out by photographers that performed colonial photography and launched the pathways for further investigation focusing the working methods used by colonial photographers.

By performing the molecular assessment of the set of negatives selected for this study it was possible to explore the topics presented above.

Regarding the identification of of negatives' film supports from historical collections, FTIR analysis allowed to identify three types of supports: cellulose nitrate, cellulose acetate and cellulose acetate butyrate. Additionally, a correlation between notch code and a European producer, Ferrania, was made. By correlating the large survey of notch code with an accurate identification of the film supports a significant improvement was accomplishing by allowing caretakers to, base on these results, perform a straightforward identification of the negatives. In this way, it is also expected to prevent cartakers of being exposure to toxic solvents and acidic acids during the identification and assessment of the negatives.

Additionally, FTIR and Raman analysis allowed to identify the different plasticizers present in the composition of the film supports analysed. For this particular issue, Raman analysis have given insighfull information about films composition.

According to the literature review, for each type of film support, beside DS, and plasticizers, few differences are pointed out (Chapter 2). Based on FTIR results obtained for cellulose nitrate-based negatives naturally aged and artificially aged samples, a trend on degradation was found, by confirming that negatives with large formats (sheet films) tend to severely degrade, losing their chemical and physical properties. Comparatively, negatives with the medium format shown to be chemically more stable. Moreover, as discussed, despite the similar molecular decay found in a few negatives with 60mm and sample from MN collection, it was confirmed that films with 60mm format are more stable and keep their physical properties. These findings were confirmed by results obtained with the artificial ageing test. Additionally, it is suggested that for ECC collection the storage and developing conditions used by the photographer during the expedition time has/ have contributed to the preservation condition of the collection.
Overall, similar behaviour was found for cellulose acetate-based negatives with large formats. Moreover, insignificant spectral changes were found in negatives with CAB support confirming that, after several decades since their production, those are well preserved. The data presented in Chapter 2 about CAB moisture regain, as well as other chemical and physical properties supports these results.
Additionally, FTIR analysis allowed to identify a 'risk group' within the cellulose acetate samples, which is visually characterized by a 'U' notch code and blue and brown hues. For this set of negatives, significant molecular degradation was found, indicating the total breakdown of the polymer (deacetylation and chain scission). Again, the data presented support the possibility of these nagatives being CDA films produced by Agfa until 1955. The presence of blue hues on the anti-halation reinforce the possibility of this films being from Agfa.

The Near-IR analysis shown the potential of this analytical technique for the identification and assessment of film-based negatives. However, a correlation between spectra with the type of film support and preservation condition was inhibited due to the contributions of the gelatine layer, the presence of anti-halation dyes regenerated and chemical corrective treatments. Moreover, the high noise and loss of resolution of the bands caused by scratches and thickness also difficulted the interpretation of the spectra obtained.

Considering pH measurements, by using micro-electrodes it was possible to assess several areas of the negatives without collecting samples or damaging the negatives. Overall, the results obtained reflect the film support decay as well as the chemical condition of the gelatine. By comparing the results for the overall set of samples, it was concluded that the chemical compounds used in corrective treatments of the image (especially Cr) and blue anti-halation dyes contribute for the low pH measurements obtained.

Regarding hardness measurements, the positive correlation obtained between hardness and molecular changes found on both naturally (CN and CA supports) and artificially (CN supports) aged samples, allow to propose this tool for assessment of the condition of film-based negatives. This finding is of extreme importance considering the effectiveness of the method and taking into account the affordability and implementation of this method.

Overall, the case studies selected for this study are representative of Portugal's photographic heritage since they represent some of the most common uses of film-based negatives used between the 1930's and 1950's. This study does not cover the numerous photographic applications or collections held by Portuguese institutions, nevertheless, it contributes to the disclosure of the photographic collections in Portugal and launches the pathway for future work.

The findings obtained with this work allow to conclude that there is a strong relationship between thickness and film decay. Moreover, it became clear that there is a type of negatives that consistently decay and jeopardizes other negatives and the entire collection. These two issues had never been interventioned until now. Additionally, with this work it was possible to propose hardness measurements as a non-destructive method to assess the film decay. This is of extreme importance since, in a preservation perspective, this is a low-cost solution that might be used by persons with different education backgrounds without detriment or difficulty to evaluate the results.
In addition, this equipment has the advantage that it can be used over a long period of time, requiring only maintenance. In this way, the need to periodically acquire more material is avoided, reducing the costs associated with the assessment of films.

Future work

In order to understand the different degradation behaviours of cellulose ester-film-based negatives produced in Europe, a broad and insightful research on the history of the industrial production of those is demanded. In this way, it might be possible to find degradation trends and, based on that findings, establish preservation strategies that will suit the necessities of European institutions responsible for the safeguard of such valuable heritage. This information could also be useful to complement the work already performed and disclosed by American institutions.

To understand the role of plasticizers for chemical and physical stability of film-based negatives, future work must be done to identify the plasticizers and quantify their concentration on the course of the film supports' decay.

Aiming to improve the assessment of the negatives by pH measurement, the contribution of gelatine for the stability of cellulose nitrate films should also be investigated.

Considering the results obtained for a set of negatives with blue anti-halation dyes, the contribution of the different anti-halo dyes for decay cellulose acetate-based negatives should also be investigated.

Given the data obtained with Raman analysis, the overall set of samples selected for this study should be analysed with this technique to assess films' condition and identify plasticizers. This data can then be compared with hardness and pH measurements already obtained and build an extensive database that may support the definition of degradation markers.

To contribute for the definition of markers, studies focusing on the molecular weight distribution should be performed in order to support the findings accomplished in this study.

In order to develop a fast an accurate method for identification and characterization of negatives with cellulose ester supports, after full characterization of variables found in the sample set studied (anti-halation dyes, gelatine layer behaviour, plasticizers), more work should be carried out to correlate the results with NIR analysis performed.

Regarding pH measurements and chemical compounds found on the image layer of negatives from ECC collection, more work should be done to confirm the contributions of those compounds for pH. Additionally, the possible contributions of metal ions for gelatine and film supports decay should be investigated.

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Appendix I Corrective treatments of the image

I.1. Image manipulations

I.1.1. Intensification and reduction

Light conditions and spectral sensitivity of photographic emulsions are crucial factors to capture an image. Inadequate light conditions may result in overexposed or underexposed photographic negatives. The lack of density and contrast may also result from specific spectral sensitivity of each type of photographic emulsion (Lavédrine and Garnier 1989; Nebblet 1952a). Since late 19th century throughout the 20th century, photographic emulsions were gradually improved, mainly to optimize the sensitivity of silver emulsions to the all spectral range. Table I.1 summarizes the several types of black and white photographic emulsions according to their spectral sensitivity.

Table I.1 - Summary of types of photographic emulsions according to their spectral sensibility (Nebblet 1952a; Adams 2005; Glafkidès 1987a, 795–96).

Type of photographic emulsions	Sensitivity range	Remarks
Violet - Blue Sensitive	~380-420 nm	Early photographic materials
Orthochromatic (green) and Isochromatic (orange)	~380 – 590 nm	Photographic negatives
Panchromatic (violet - orange)	~380-725 nm	Photographic negatives

Corrections on image density and contrast are performed by intensification, reduction or reinforcement corrective treatments. Reduction and intensification treatments are used to produce fundamental changes in previously developed images from negatives. Reduction or "weakening" solutions act as oxidation reactions that promote the decrease of the optical density of the images. Inversely, the intensification treatments are used to increase the optical density. The main goal of both methods is to correct image defects caused by improper exposure or development of the negatives.
Reinforcement and intensification treatments are similar in the action however the former is performed in latent images and the later on developed images of photographic negatives (Glafkidès 1987b).

Reduction and intensification treatments are selected according to the following criteria: image benefits and permanency of the processes; applicability to several types of

emulsions; no risk of discolouration or staining; no risks of causing degradation of the gelatin, and, also absence of any action that could change images' grain (Neblette 1952).

Reduction and intensification are classified according to the nature of the solution and action of each solution. Based on that two broad types of methods are proposed: one that can act proportionally on the density of the image and will change the gamma of the image (*proportional methods*), and another that does not act in images' gamma and will act independently on the density (*independent method*).

In the following sections several reduction and intensification solutions are presented.

I.1.1.1 Reduction treatment

Reduction, is based on an oxidation reaction that promotes the remotion of some metallic silver to decrease opacity or optical density of the image achieved by a chemical treatment (Mees 1942b; Neblette 1931b). For that, all the reducing agents must be able to perform the oxidation of silver into a soluble salt that may be dissolved away (Nebblet 1931; Mees 1942b). In Table I.2 a summary of reducing agents and adequate solvents used in reduction solutions are presented (Mees 1942b).

Table I. 2 – Reducing agents and the adequate solvents that will dissolve the salts formed during the reduction process (Mees 1942b)

Reducers or oxidizing agents	Complexing/coordination agent	Soluble salt
Permanganate Dichromate Ferric ammonium sulfate Ceric Persulfate	Sulfuric acid	Silver sulfate
Ferricyanide	Thiosulfate or thiocyanate	Ferrocyanide
Iodine	Cyanide	Silver iodide

According to the type of action and changes promoted on the image, three reduction classes are proposed: a) *subtractive* and *subproportional*, b) *proportional*, and c) s*uperproportional* (Table I.3) (Nebblet 1931; Mees 1942b).

Table I. 3 – Types of reduction treatment, other designations according with the type of reduction action, remarks related with each reduction class and performance on density and contrast, and examples of reduction solutions (Nebblet 1931; Mees 1942b)

Reduction Class	Other designations	Remarks	Examples
Subproportional	Surface cutting or cutting reducers	Higher reduction ratio for low densities than for higher densities	- Potassium Ferricyanide-thiosulfate (Farmer's); - Ferricyanide-thiocyanate (Haddon's); - Iodine-cyanide; - Potassium ferric chloride-acid-oxalate-thiosulfate (Belitski); - Potassium permanganate-sulfuric acid; - Dichromate-sulfuric acid; - Ceric salts with nitric or sulfuric acid; - Cupric chloride-thiosulfate; - Mercury and cyanide (Eder's).
Subtractive		Reduce all densities by equal amount giving more contrast to the image	
Proportional	Progressive, true scale	Reduces all the densities in the same ratio without contrast alterations	- Potassium permanganate ammonium sulphate with sulphuric acid (Nietz & Huse) ; - Potassium permanganate (alone or with weak acid); - Permanganate-persulphate with sulphuric acid; - Ferric ammonium sulphate with sulfuric acid; - Quinone with sulphuric acid
Superproportional	Flattening Persulphate	Higher reduction ratio for greater densities than for lower densities, giving less contrast	- Ammonium or potassium persulfate alone or with sulphuric acid; - Ferricyanide-bromide bleach, non-staining partial redevelopment followed by fixing; - Dichromate-potassium bromide-hydrochloric acid bleach, non-staining partial redevelopment followed by fixing

Subproportional and subtractive reduction treatments are subdivisions of the subtractive class (Table I.3). The separation of these two methods is based on the action performed on the image density. The subproportional methods act mostly on the low densities of the image, while the subtractive methods act equally in the overall density and improves contrast. Like subtractive treatments, proportional treatments are applied whenever an equal reduction of the overall density is required. However, in opposition the proportional methods do not change the image contrast. Superproportional methods are selected whenever it is necessary to perform a higher reduction of higher densities in the images (Nebblet 1931).

The reduction solutions are named according to the salts and oxidizing agents, or according to their inventor's name. Some oxidizing agents may be found in different reduction classes as is the case of permanganate (Table I.3). Permanganate is a strong oxidizing agent introduced by R. Namias, was used as the potassium salt alone or in the presence of a weak or a strong acid. Potassium permanganate in the presence of sulphuric acid will oxidize silver and form silver sulphate (a water-soluble compound) (Nebblet 1931). According to C. B.Nebblet (1931,1952) and C. E. Kenneth Mees (1942b), Namias reaction is as follow:

$$5Ag_2 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Ag_2SO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

Iron is also an element used for reduction solutions, e.g. for Farmer's, Haddon's and Belitski subtractive solutions (Table I.3). Farmer's is pointed out as the most common and satisfactory solution. Containing potassium ferricyanide and thiosulfate, this solution is highlighted as a *vigorous* solution used to improve lower densities and promote strong contrast (Nebblet 1931; Mees 1942b). The ferricyanide oxidizes the silver image, forming silver ferrocyanide. The latter is dissolved by the thiosulfate (hypo) fixer. The following reaction is proposed for Farmer's solution (Neblette 1952):

a) $4Ag + 4K_3Fe(CN)_6 \rightarrow Ag_4Fe(CN)_6 + 3K_4Fe(CN)_6$

b) $3Ag_4Fe(CN)_6 + 16Na_2S_2O_3 \rightarrow 4Na_5Ag_3(S_2O_3)_4 + 3Na_4Fe(CN)_6$

Mees (1942b) adverted to the instability of ferricyanide-thiosulfate solutions, which is caused by the oxidation of the thiosulfate by ferricyanide (Mees 1942b).

For Haddon's solution, with ferricyanide and thiocyanate, the proposed reaction is the following (Neblette 1952):

1. $4Ag + 4K_3Fe(CN)_6 \rightarrow Ag_4Fe(CN)_6 + 3K_4Fe(CN)_6$
2. $Ag_4Fe(CN)_6 + (x+4)NH_4CNS \rightarrow xNH_4CNS \cdot 4AgCNS + (NH_4)Fe(CN)_6$

With Belitski solution it is possible to obtain images with similar results to those obtain with Farmer's. This solution is also known as potassium ferric chloride-acid-oxalate-thiosulfate solution (Table I.3). For these three iron-based methods, silver oxidation is performed differently. In Farmer's and Haddon's solutions silver is oxidized by ferricyanide, while with Belitski's, the silver oxidation is performed by the oxygen held by the iron salts, resulting in silver oxide that is dissolved by the thiosulfate (Nebblet 1931; Mees 1942b).

A high percentage of reduction solutions are based on the use of permanganate or iron (Table I.3). However, there are other solutions in which mercury, dichromate, bromide and iodine are used as oxidizing agents. Eder's, or mercury and cyanide, solution has a similar action to Farmer's, however the solution is not so vigorous, having the advantages of a slow action rate and being a non-staining solution. However it is also known for its poisonous character, which was its major drawback (Nebblet 1931).

The iodine-cyanide solution is indicated as a solution to "work" on the high densities of the image and is also reported for its extensive action on low densities hence causing changes in shadows. This is a subtractive non-acid solution appreciated due to its non-staining properties. However, this solution has the drawback of being poisonous. In the iodine-cyanide solution, iodine is the reducer and cyanide is the complexing agent that will dissolve the silver iodine formed during the reaction (Neblette 1952). For iodine-cyanide subtractive method, the reaction proposed is (Neblette 1952):

$$2Ag + I_2 + 4KCN \rightarrow 2KAg(CN)_2 + 2KI$$

Besides the presented subtractive reducing solutions, there are also the proportional and superproportional reduction solutions (Table I.3). As mentioned previously, these two classes are differentiated based on the type of action performed on the image and reduction solutions used to perform those actions (Neblette 1952; Nebblet 1931; Mees 1942b). The superproportional methods are applied when the goal is to reduce contrast performing a tailored printing matrix for printing mediums with special spectral sensibilities (Nebblet 1931). Within the superproportional reducers, ammonium and potassium persulfate, ferricyanide-bromide and dichromate-potassium are indicated as oxidizing agents (Table I.3) being ammonium persulfate the most effective one (Nebblet 1931; Mees 1942b). Ammonium persulfate is considered to have an unreliable and speculative action, caused by the presence of acids and silver ions that may accelerate the action of the reducing solution, resulting in an irreversible performance on image densities and contrast (Neblette 1931a; Mees 1942b). The proportional and superproportional action of the persulfate has been discussed by several authors. Considering the action of persulfate two theories, the *dispersoid theory*, defended by Lüppo-Cramer, and the *catalytic theory*, defended by Schuller, Stenger and Heller are presented (Neblette 1931).

In the *dispersoid theory* it is proposed that image deposits are a combination of metallic silver and silver bromide. Comparatively, metallic silver is more soluble in persulfate than silver bromide. This means that the nature of the superproportional action of persulfate changes according with the type of silver which forms the image, and consequently acquires a superproportional or proportional character (Nebblet 1931). The proportional action relies on the performance of silver bromide solvents which will act first on halides by preparing the action of persulfate on the metallic silver (Nebblet 1931). Proportional solutions are obtained by combining subtractive reducers with superproportional reducers (Nebblet 1931). As presented in Table I.3, there are three proportional reduction solutions with ammonium persulphate or sulphate combined with potassium, potassium permanganate or iron.

The action of a proportional reducer depends on the appropriate combination of ammonium persulfate with potassium permanganate and sulphuric acid (Nebblet 1931). As a superproportional reducer, the catalytic reaction theory is based on persulfate's superproportional action and its catalytic effect on the silver ions formed during the reaction. It is also said that this reaction can become autocatalytic in the presence of other substances (impurities) (Mees 1942b). The presence of iron (in commercial

solutions), chlorides, bromides, sulphates and nitrates (present in nontreated water) and copper ions have an important role on the autocatalytic action of persulfate reducers (Nebblet 1931; Mees 1942b). The velocity and the extent of the reaction depends on these variables (Mees 1942b).

Due to the speculative reaction of persulfate, Neblette (1952) presents a simple equation for a persulfate reduction method

$$2Ag + (NH_4)_2S_2O_8 \rightarrow Ag_2SO_4 + (NH_4)_2SO_4$$

According to Neblette the acid content increases during reduction and consequently the rate of the reaction increases by the hydrogen ion and silver. This phenomenon was also studied by Sheppard and by Higson, and both proposed similar equations for the following reactions (Nebblet 1931).

Summarizing, image reduction is performed with oxidizing solutions, in which different reducers (reduction agents) and solvents, combined, play their role. Two oxidation paths are possible to achieve image improvement, and both rely on salts solubility. One path is based on the conversion of silver into a soluble salt and the other path is based on the performance of solvents on silver salts which are insoluble on water. Therefore, cyanide dissolves the silver iodide formed with the iodine reduction method. In Farmer's and Haddon's methods the solvents thiosulfate and thiocyanate are used to dissolve the silver ferrocyanide. Sulphuric acid is used to dissolve silver as silver sulphate in which permanganate, ferric ammonium sulphate persulfate, ceric and dichromate are used (Mees 1942b).

The reduction process is not linear and, chemically, some risks are taken without any reliability for the image and negative preservation. Options are made according to the degree of reduction desired. The action of some reducers may sometimes be adverse for the photographic emulsion, as for example the permanganate-persulfate method, which may soften the gelatine and promote the formation of stains (Nebblet 1931).

There are several examples of stains and discolorations caused by reduction processes or impurities present on water used for washing negatives. Green and blue stains are attributed to ferricyanide reducer or to chrome alum fixing solution. However blue stains are also related to the presence of iron in water (Lester 1946; Eaton et al.1985). The lack of practical knowledge and inadequate performance of reduction actions can lead to the need of chemical baths to remove stains, as is the case of the removal of brown deposit of manganese oxide formed by an acidic permanganate solution using a fixing bath of sodium sulphite (Nebblet 1931).

I.1.1.2 Intensification treatment

Inversely to reduction treatments, intensification treatments were used to increase image density and contrast mostly on underdeveloped and overexposed negatives (Nebblet

1931; Mees 1942b). As Mees (1942b) referred, density and contrast are increased through "[...] *adding to the silver image, by partially or entirely replacing it by an optical denser material or by altering the photometric constant*."

Intensification treatments are grouped in three classes: *subproportional*, *proportional*, and s*uperproportional* methods (Table I.4).

Table I.4 – Intensification classes, remarks for each intensification class concerning the performance on density and contrast, and examples of intensification solutions (Nebblet 1931; Mees 1942b; Lavédrine and Garnier 1989)

Class	Remarks	Intensifiers
Subproportional	Whenever the increasing of density decreases with increment of the original density	– Uranium salts; – Chromium salts with incomplete bleaching or redevelopment; – Ferric-bromide bleach in combination with staining redeveloper and incomplete bleaching or redevelopment; – Mercuric iodide followed by a *p*-aminophenol redeveloper; – Mercuric iodide, sodium sulphite solution (Lumiére Brothers)
Proportional	Increasing of the density proportionally to original density	– Chromium salt (dichromate-hydrochloric acid bleach; metol-hydroquinone redeveloper) – Mercuric chloride-bromine bleach; silver potassium cyanide redeveloper (Monckhoven's) – Mercuric chloride, sodium thiosulfate, potassium iodide solution (Kirchoff's) – Silver salts
Superproportional	Whenever the increasing of the density follows the increasing of the original density	– Monckhoven's intensifier with slight excess of potassium cyanide in the redeveloping solution. – Mercuric bromide bleach; sodium sulphite redeveloper.

Intensification methods may also be grouped according to the type of action performed, being summarized in three categories: *physical, chemical* and *optical intensification* methods.

Physical and chemical intensification methods act on the improvement of the image by increasing its density, or in other words by increasing the mass of the image through the deposition or addition of other compounds (Nebblet 1931; Neblette 1952; Mees 1942b). The *physical method* is a redeveloping process based on the action of a developing solution that contains a silver salt, and a developing agent that, in an acidic or alkaline solution will reduce the silver salts to metallic silver. This reaction will cause an increasing of density due to nuclei performance of the grains of the original silver image, which promote the deposition of the reduced silver (metallic silver) into the original image (metallic silver) (Neblette 1952).

The *chemical method* is based on the addition of silver or other metal compounds, such as chromium or mercury to the image. Intensification with chromium is preceded by image bleaching, and intensification with mercury is based on bleaching and blackening (darkening) of the image (Neblette 1952). The bleaching solution is based on the action of a soluble salt that will attack metallic silver and form a mixture of an "[...] *insoluble silver compound, and an insoluble, reduced salt.*" (Mees 1942b). The opacity of these compounds is achieved with a developer, sodium sulphite, or ammonia (Mees 1942b, 552).

Chromium is one of the intensifiers pointed out for chemical intensification (Nebblet 1952b; Neblette 1952). According to the literature, intensification with chromium is performed with a bleaching solution of acid dichromate (dichromate-hydrochloric acid bleach).The reaction proposed is (Neblette 1952):

$$2Ag + K_2Cr_2O_7 + 2HCl \rightarrow 2AgCl + CrO_2 \text{ or } Cr_2Cl_2$$

CrO_2 and Cr_2Cl_2 are products of the reduction of dichromate. The development with a common developer (metol hydroquinone) will reduce silver chloride to silver, and consequently, the density will increase. This means that with chromium intensification the density of the image increases according to the amount of the added chromium compound (Nebblet 1931; Neblette 1952).

Besides chromium, mercury is is also highlighted. Three intensification processes based on the action of mercury are presented in Table I.4: mercuric iodide (an intensification solution with two possible developers), mercuric chloride (Monckhovens' in which different amounts of potassium cyanide may be used) and the mercuric bromide. The bleaching of the image is performed with mercuric chloride (Monckhoven) and mercuric bromide (Neblette 1952; Mees 1942b). The mercuric ion will attack metallic silver and form silver chloride and a mercurous salt. The reaction is:

$$2HgX_2 + 2Ag \rightarrow Hg_2X_2 + 2AgX \qquad X = Cl, Br$$

In order to yield opacity a blackening or darkening step is further required. Blackening may be performed with different developers, such as sodium sulphite, ammonia, ferrous oxalate and silver cyanide. The possible reactions are presented below (Neblette 1952; Nebblet 1931):

a. *Sodium sulphite*

$$Hg_2Cl_2 + Na_2SO_3 + H_2O \rightarrow 2Hg + Na_2SO_4 + 2HCl$$

b. *Ammonia*

$$Hg_2Cl_2 + 2NH_3 \rightarrow NH_2Hg_2Cl + NH_4Cl$$

c. *Ferrous oxalate*

$$Hg_2Cl_2 + 2AgCl + 4FeC_2O_4 + 2K_2C_2O_4 \rightarrow 2Ag + 2Hg + 2Fe_2(C_2O_4)_3 + 4KCl$$

d. *Silver cyanide*

$$Hg_2Cl_2 + 2AgK(CN)_2 \rightarrow 2Ag + 2Hg(CN)_2 + 2KCl$$

A bleaching of the image is the first step for the mercuric bromide (Monckhoven's) method, as described above. The blackening step is done with a solution of potassium cyanide and silver. For Monckhoven method is proposed the reaction (Nebblet 1931):

$$Hg_2Cl_2 + 2AgK(CN)_2 \rightarrow 2Ag + 2Hg(CN)_2 + 2KCl$$

From the mercury intensifiers group, the mercuric iodide method was commonly used as an alternative due to its single solution procedure. Neblett pointed out to the behaviour of this method, which, compared with others, do not change with residues of thiosulfate. The results achieved with this corrective treatment, overall, more homogeneous, not being reported the formation of stains in the image. Nebblet (1931;1952) proposed the following reaction for this method (Nebblet 1931; Neblette 1952):

$$2HgI_2 + 2Ag \rightarrow Hg_2I_2 + 2AgI,$$
$$Hg_2I_2 + 2Na_2SO_3 \rightarrow Hg + HgI_2 \cdot (Na_2SO_3)_2$$

The permanence of the image also constituted a problem and could only be achieved by a total reduction or conversion of the image into metallic mercury and silver (Neblette 1952; Mees 1942a). A colour alteration is reported for mercury iodide method. During the intensification, process colours change from a neutral (metallic silver) to brown (solution action on silver), to orange (washing bath) to yellow (re-development with amidol or metol-hydroquinone) (Nebblet 1931).

In sum, *chemical and physical intensifiers* promote changes on the mass of the images by adding metallic silver or other metal compounds. However, there are other intensification methods that could be used, which would cause changes in the colour of the image. The intensification methods with uranium and sulphide, also called *toning solutions*, are given as examples for the formation of "*a more non-actinic colour*" materials (Nebblet 1931). These are *optical intensification* corrective treatments through which it is possible to increase opacity without promoting any changes on the mass of the silver image, but rather on the colour that the image obtains with the intensification treatment (Nebblet 1931; Mees 1942b).
In the process, a negative is bleached and redeveloped to increase opacity and contrast, reached by the resulting colour (yellow-brown) that will act as a "filter" for printing on papers sensible to blue-and-violet light (Neblette 1952; Mees 1942b). For example, the bleaching of a silver image with ferric bromide (oxidizing solution), will give a silver bromide image that when darkened (redeveloped) with sodium sulphite will render silver sulphite, resulting in a less dense brown image. The colour obtained is directly correlated with the increment of opacity, resulting in a higher contrast. The colours that metallic silver images may acquire are related to the type of blackening performed. The brown colour is associated to sulphide, red colour to chromate and buff (light brown-yellow) colour to ferricyanide. Apparently, all types of intensification methods promote the formation of colours and, sometimes also stains. These changes rely on the type and

degree of intensification and dimension of the image grain. Nevertheless, the formation of stains is commonly correlated with residues of thiosulfate and incorrect washing (Eaton et al.1985,74-5).

As previously discussed, in some situations, image improvements are the only options for photographers to "save" an image and do an excellent print. Image improvements are a broad subject that cannot be completely discussed in this work, since there are innumerous options to perform changes in images (Tables I.2, I.3 and I.4).

In this study, some of the most common options are presented. Nonetheless, there are other methods, so-called *miscellaneous*, where a) intensification and reduction are combined; b) where the silver image is converted into a mordant for dyes; and c) an intensification or reduction of a specific part of the negative is performed (*local* intensification or reduction) (Nebblet 1931; Neblette 1952; Mees 1942b). These methods are described as optional and are not presented or discussed in this work.

Reduction and intensification formulas, applications and potencial problems have been described. The color changes, stains and defects caused by each type of process have been reported and are found to be one of the several indicators of the performance of image improvements. Some authors do a clear attribution of a color to a specific intensification or reduction process, for example: iron is commonly related to blue stains, quinone (developer) residues is associated with brown hues and mercuric iodide intensification is associated intense yellow hue on the image (Wall 1924; Neblette 1952; Lavédrine and Garnier 1989). It was also pointed the poisonous character of some of the image improvement formulations such as those that use mercury, chromium lead or uranium (Neblette 1952).

I.1.2. Image retouching, masking and coating

Beside chemical treatments, photographers retouched, masked and coated the negatives to provide protection or for practical functions (e.g. correction of flaws) (Norris and Kennedy 2005, 13).
By coating[125] the photographic emulsion, photographers were protecting the image and preparing the substratum for retouching.
The image was retouched or masked whenever imperfections or flaws were found, therefore correcting and improving the image for printing (Pederson et al. 2005, 109,113).
The retouching procedure was preceded by coating the image. A broad type of coating materials was used, ranging from natural resins to CN lacquers (Pederson et al. 2005).
The common medium used for retouching photographic negatives was a mixture of turpentine and gum dammar (tradename *Mattolein*) (Valverde 2005, 21; Pederson et al. 2005, 113). Besides dammar, other materials and solutions were used according to compatibility and final goals, being cold lacquers such as dammar benzene, Zapon

[125] Besides coating, varnish and lacquer were two other designations used by photographers (Pederson et al. 2005).

lacquer, shellac in alcohol, shellac in water-borax, glycerine and *Mattolein* mostly used for coating CN photographic negatives (Pederson et al. 2005, 118; Valverde 2005, 21). With respect to CA film-based negatives, no references to procedures or coating materials were found.

Additionally, beside the corrective treatments aforementioned, image masking was performed. This action was performed mostly on areas of the image that required *less exposure*, or to screen parts of the image that were not to print (Pederson et al. 2005, 115). An example of masking is presented in Fig. 2.13. The masking intervention was mostly performed in orthochromatic glass plate negatives and early films (Pederson et al. 2005, 115). Commonly, dyes such as Neo-coccine or Vanguard yellow were used for masking since those would act as filters blocking light in specific areas on the image, and being very useful for printing (Valverde 2005, 21).

Appendix II – Notch codes

Notch codes presented in the literature for film-based negatives.

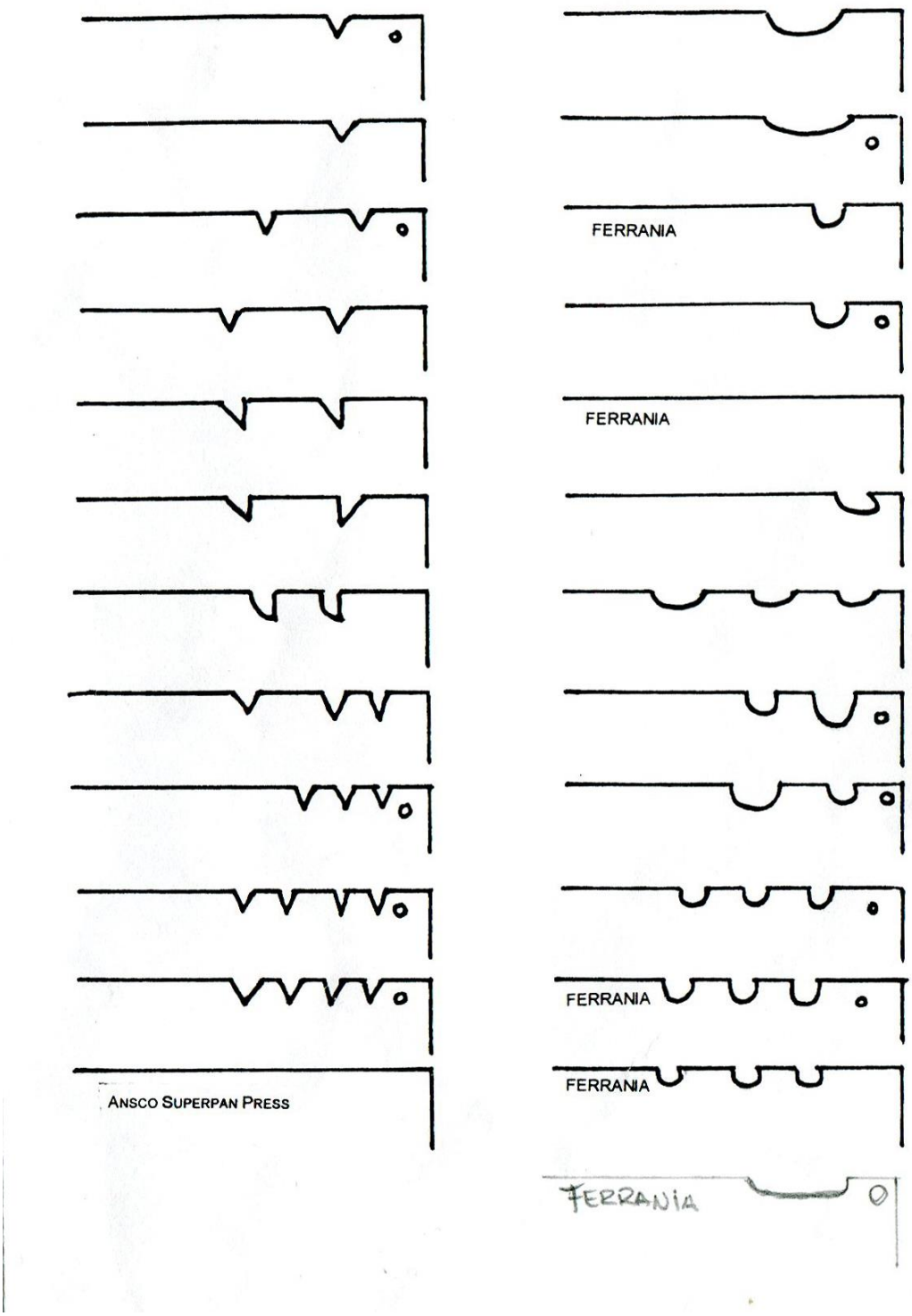


Figure II.1 – Notch codes for cellulose nitrate-based negatives surveyed by several teams from Luis Pavão Lda.

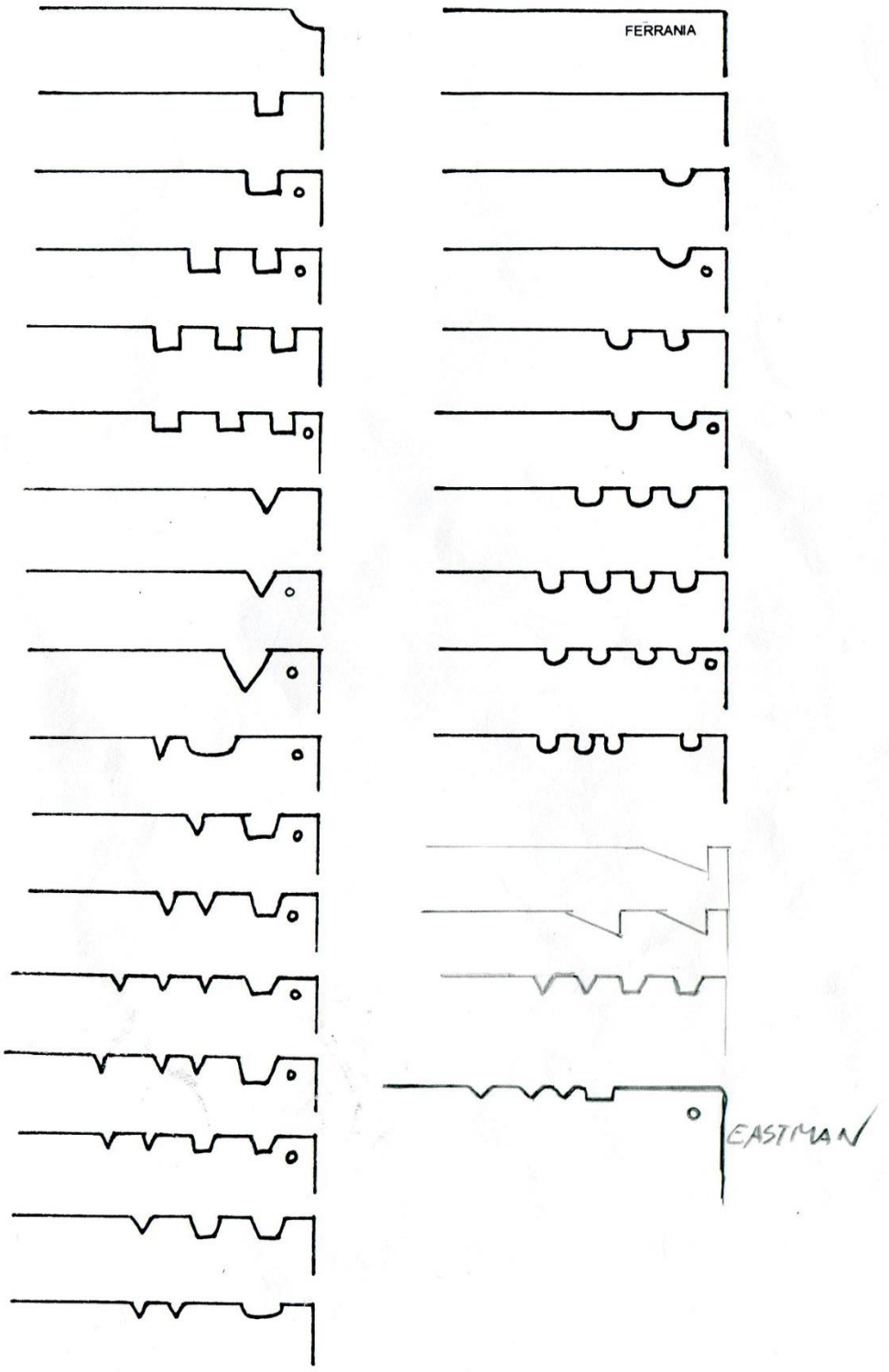


Figure II.2 – Notch codes attributed to cellulose acetate-based negatives surveyed by several teams from Luis Pavão Lda.

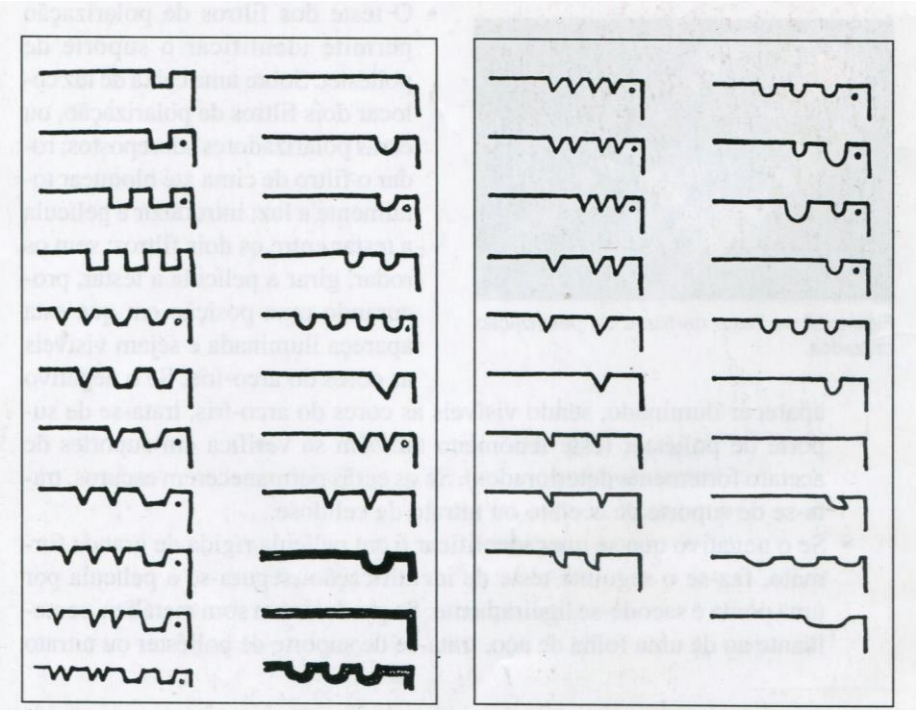


Figure II.3 – Notch codes for sheet films with cellulose acetate base (left) and cellulose nitrate base (right) (Pavão, 1997).

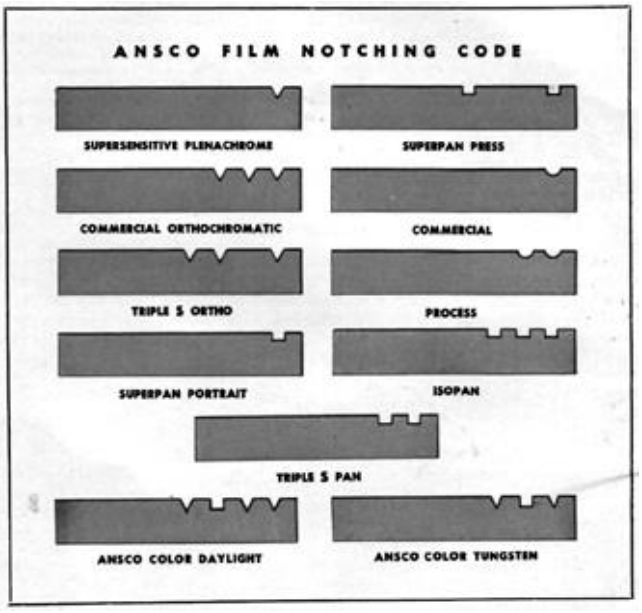


Figure II.4 – Survey of notch codes used in ANSCO films[126]

[126] References taken from the website http://johnesimmons.com/?p=1438 (access February 2017).

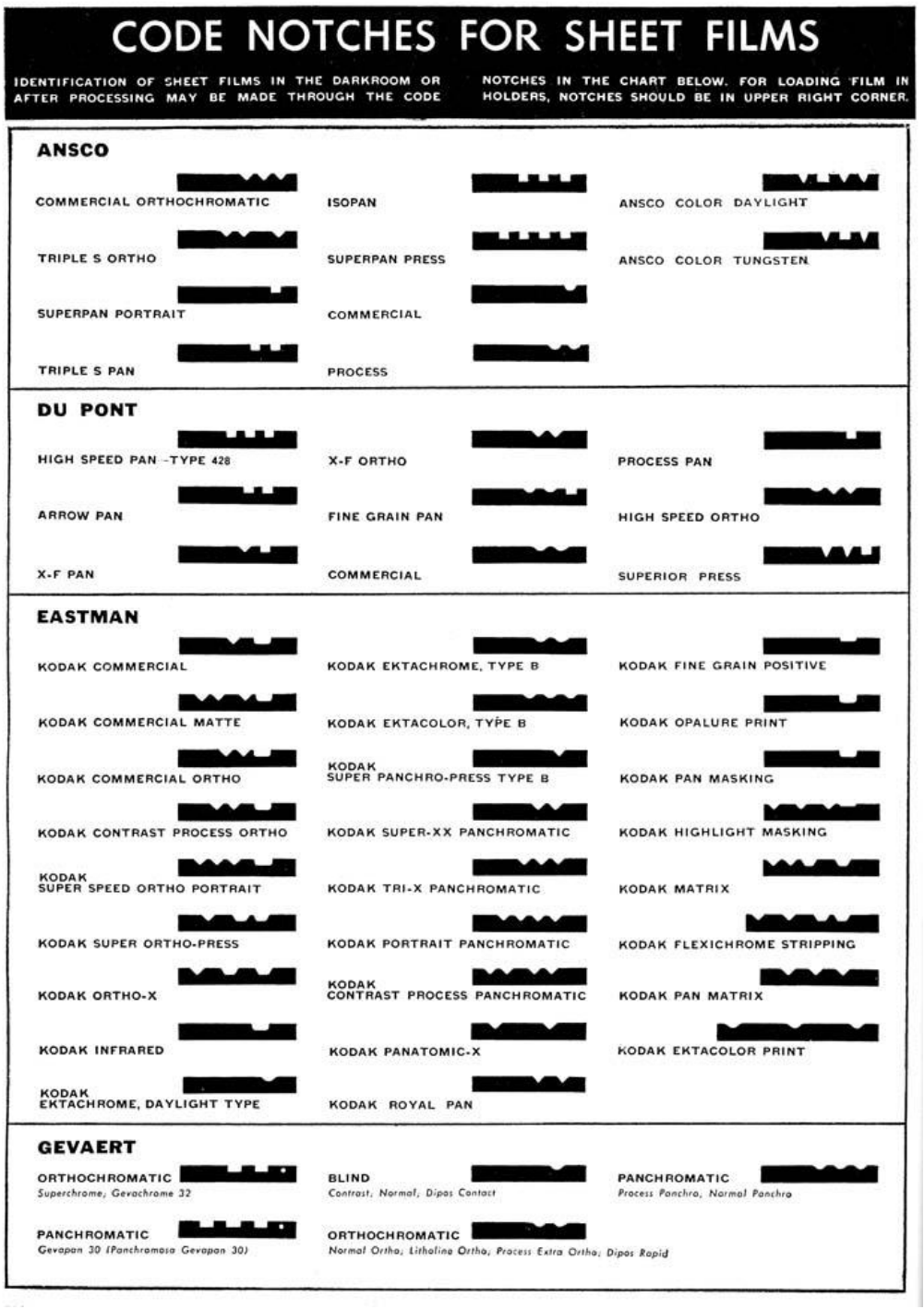
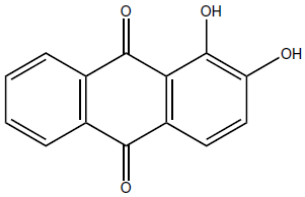
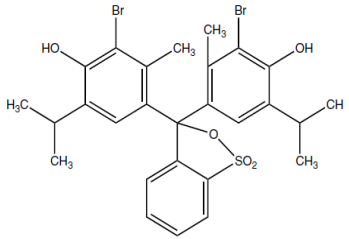


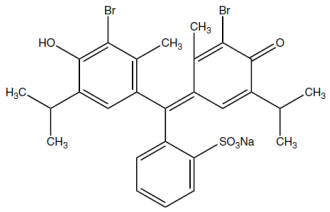
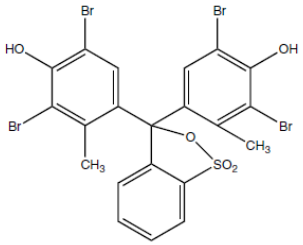
Figure II. 5 - Survey of notch codes used in sheet films from ANSCO, Du PONT, EASTMAN and GEVAERT[127].

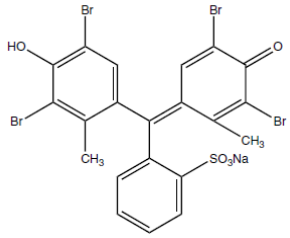
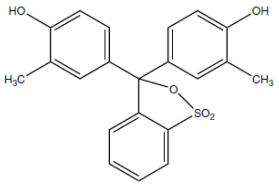
[127] References taken from the website http://static.photo.net/attachments/bboard/00S/00S1f0-104051084.jpg (access February 2017).

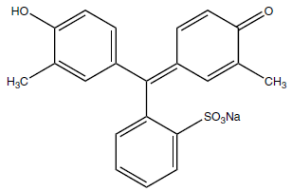
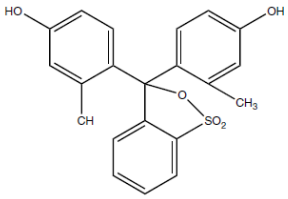
Appendix III – Dyes

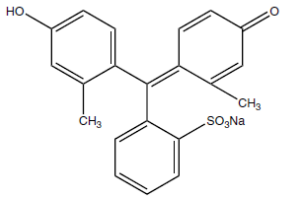
Table III.1 – Information about dyes used for colorimetric methods for assessment of cellulose nitrate and cellulose acetate film-based negatives*: IUPAC* identification, chemical formula, chemical structure, acidity, pH range, range of colour and references. General remarks on dyes used as pH indicators.

Dye	Chemical formula	Chemical Structure	Acidity (pK_a)	pH range	Colour change at pH	References
Alizarin red IUPAC name: 1,2-dihydroxy-9,10-anthracenedione Chemical dye class: Miscellaneous, Anthraquinone Molecular weight: 240.21	$C_{14}H_8O_4$		6.77	5.5 – 6.8; 10.1 – 12.1	Yellow (5.5) to red (6.8) Red (10.1) to purple (12.1)	(R. W. Sabnis 2008)
Bromothymol blue IUPAC name: 4,4′-(1,1-Dioxido-3*H*-2,1-benzoxathiole-3,3-diyl)bis(2-bromo-6-isopropyl-3-methylphenol) Chemical dye class: Sulfonephthalein Molecular weight: 624.38	$C_{27}H_{28}Br_2O_5S$		7.0, 7.1	6.0 – 7.6	Yellow (6.0) to blue (7.6)	(R. W. Sabnis 2008)

Dye	Chemical formula	Chemical Structure	Acidity (pK_a)	pH range	Colour change at pH	References
Bromothymol blue, Sodium salt IUPAC name: Chemical dye class: Sulfonephthalein Molecular weight: 646.38	$C_{27}H_{27}Br_2O_5SNa$		7.0, 7.1	6.0 – 7.6	Yellow (6.0) to blue (7.6)	(R. W. Sabnis 2008)
Bromocresol green IUPAC name: 2,6-Dibromo-4-[7-(3,5-dibromo-4-hydroxy-2-methyl-phenyl)-9,9-dioxo-8-oxa-9λ6-thiabicyclo[4.3.0]nona-1,3,5-trien-7-yl]-3-methyl-phenol Chemical dye class: Sulfonephthalein Molecular weight: 698.01	$C_{21}H_{14}Br_4O_5S$		4.7, 4.6	3.8 – 5.4	Yellow (3.8) to blue-green (5.4)	(R. W. Sabnis 2008)

Dye	Chemical formula	Chemical Structure	Acidity (pK_a)	pH range	Colour change at pH	References
Bromocresol green, sodium salt IUPAC name: Chemical dye class: Sulfonephthalein Molecular weight: 720.02	$C_{21}H_{13}Br_4O_5SNa$		4.6	3.8 – 5.4	Yellow (3.8) to blue-green (5.4)	(R. W. Sabnis 2008)
Cresol red (o-Cresolsulfonephthalein) IUPAC name: 4-[3-(4-hidroxi-3-metilfenil)- 1,1-dioxobenzo[c]oxatiol-3-il]- 2-metilfenol Chemical dye class: Sulfonephthalein	$C_{21}H_{18}O_5S$		1.4, 8.2, 8.3	0.2-1.8 7.0-8.8	Red (0.2) to yellow (1.8) Yellow (7.0) to reddish-purple (8.8)	(R. W. Sabnis 2008)

Dye	Chemical formula	Chemical Structure	Acidity (pK_a)	pH range	Colour change at pH	References
Molecular weight: 382.43						
o-Cresol red, sodium salt IUPAC name: 4-[3-(4-hidroxi-3-metilfenil)- 1,1-dioxobenzo[c]oxatiol-3-il]- 2-metilfenol Chemical dye class: Sulfonephthalein Molecular weight: 404.42	$C_{21}H_{17}O_5SNa$		1.4, 8.2, 8.3	0.2-1.8 7.0-8.8	Red (0.2) to yellow (1.8) Yellow (7.0) to reddish-purple (8.8)	(R. W. Sabnis 2008)
m-Cresol purple (m-Cresolsulfonephthalein) IUPAC name: 4-[3-(4-hydroxy-2-methylphenyl)-1,1-dioxo-2,1$I^{6}-benzoxathiol-3-yl]-3-methylphenol Chemical dye class: Sulfonephthalein Molecular weight: 382.43	$C_{21}H_{18}O_5S$		1.51, 8.32	1.2 – 2.8; 7.4 – 9.0	Red (1.2) to yellow (2.8) Yellow (7.4) to purple (9.0)	https://pubchem.ncbi.nlm.nih.gov/compound/73030#section=Top (R. W. Sabnis 2008)

Dye	Chemical formula	Chemical Structure	Acidity (pK_a)	pH range	Colour change at pH	References
m-Cresol Purple sodium salt IUPAC name: sodium;2-[(E)-(4-hydroxy-2-methylphenyl)-(2-methyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl]benzenesulfonate Chemical dye class: Sulfonephthalein Molecular weight: 404.42	$C_{21}H_{17}NaO_5S$		1.51, 8.32	1.2 – 2.8 7.4-9.0	Red (1.2) to yellow (2.8) Yellow (7.4) to purple (9.0)	(R. W. Sabnis 2008)

Appendix IV – Infrared and Raman peaks assignment

IV.1 Cellulose nitrate model film

Cellulose nitrate[128] (Fig. IV.1). The assignment of the main IR bands is shown in Table IV.1.

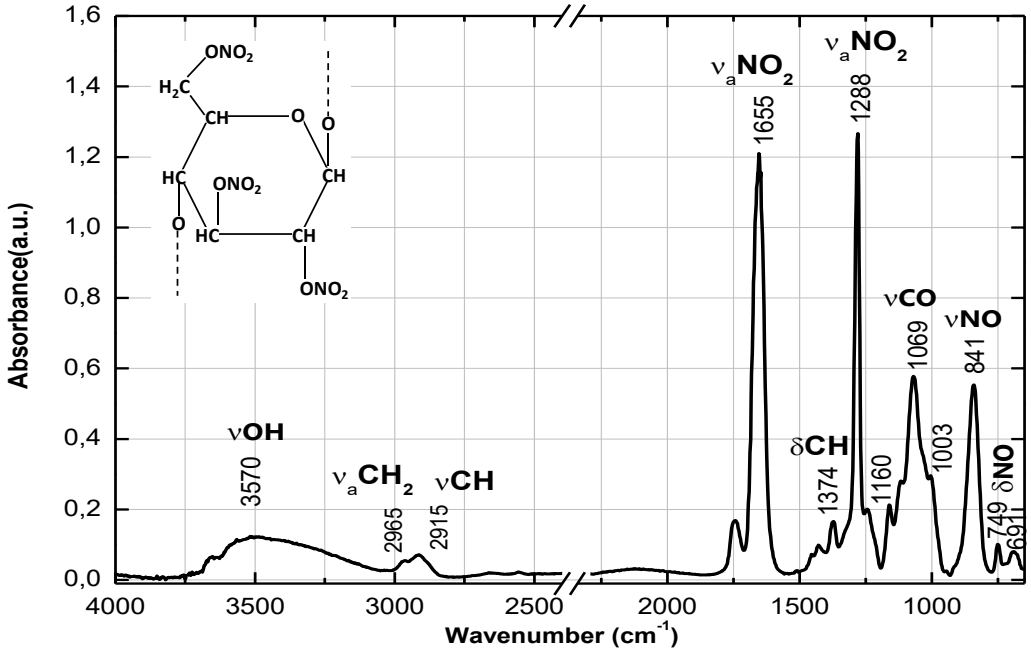


Figure IV.1 – Infrared spectrum of a model cellulose nitrate.

[128] The infrared spectrum of cellulose nitrate (14,2% nitrogen content) was acquired from the Aldrich Condensed Phase Library database. The spectra in this library is published in The Aldrich Library of FT-IR Spectra, vols. 1 and 2.

Table IV.1 Infrared assignment for cellulose nitrate

IR peaks (wavenumber, cm^{-1})	Assignment	Reference
3300 - 3500 (w)	ν(OH) (OH...O_2NO)	(Zhbankov 1966; Eisenreich and Pfeil 1983; Jutier et al. 1987; Kovalenko et al. 1956; Stewart 1997; Quye et al. 2011b; Berthumeyrie et al. 2014; Bussiere, Gardette, and Therias 2014)
2965 (w)	$\nu_a(CH_2)$	(Watanabe, Hayashi, and Iriai 1968; Eisenreich and Pfeil 1983; Jutier et al. 1987; Kovalenko et al. 1956; Stewart 1997; Quye et al. 2011a; Bussiere, Gardette, and Therias 2014; Berthumeyrie et al. 2014)
2915 (w)	ν(CH)	(Watanabe, Hayashi, and Iriai 1968; Jutier et al. 1987; Stewart 1997; Quye et al. 2011b)
	$\nu_s(CH_2)$	(Eisenreich and Pfeil 1983; Kovalenko et al. 1956)
1655 (vs)	$\nu_a(NO_2)$	(Watanabe, Hayashi, and Iriai 1968; Eisenreich and Pfeil 1983; Jutier et al. 1987; Kovalenko et al. 1956; Stewart 1997; Quye et al. 2011b; Bussiere, Gardette, and Therias 2014; Berthumeyrie et al. 2014)
1454 (w)	$\delta(CH_2)$	(Berthumeyrie et al. 2014; Bussiere, Gardette, and Therias 2014)
1425 (w)	$\delta(CH_2)$	(Watanabe, Hayashi, and Iriai 1968; Jutier et al. 1987; Stewart 1997; Quye et al. 2011a)
	δ(CH)	(Kovalenko et al. 1956)
1374 (w)	δ(CH)	(Watanabe, Hayashi, and Iriai 1968; Jutier et al. 1987; Kovalenko et al. 1956; Stewart 1997; Quye et al. 2011b; Bussiere, Gardette, and Therias 2014; Berthumeyrie et al. 2014)
1326 (w, sh)	$\delta(CH_2)$	(Watanabe, Hayashi, and Iriai 1968; Kovalenko et al. 1956)
1282 (vs)	$\nu_s(NO_2)$	(Eisenreich and Pfeil 1983; Jutier et al. 1987; Kovalenko et al. 1956; Stewart 1997; Quye et al. 2011b; Bussiere, Gardette, and Therias 2014; Berthumeyrie et al. 2014)
1160 (w)	ν(COC) glycosidic linkage	(Jutier et al. 1987; Kovalenko et al. 1956)
	ν(COC) acetal structure	(Bussiere, Gardette, and Therias 2014; Berthumeyrie et al. 2014)
	νring	(Stewart 1997; Quye et al. 2011b)
1118 (m)	ν(COC) glycosidic linkage	(Kovalenko et al. 1956)
	ν(COC) acetal structure	(Berthumeyrie et al. 2014; Bussiere, Gardette, and Therias 2014)
	νring; $\nu_s$ring	(Jutier et al. 1987);(Stewart 1997; Quye et al. 2011b)
1069 (s)	ν(COC) (C5-O-C1)	(Kovalenko et al. 1956)
	ν(COC) glycosidic linkage	(Jutier et al. 1987; Stewart 1997; Quye et al. 2011b)
	ν(COC) acetal structure	(Berthumeyrie et al. 2014; Bussiere, Gardette, and Therias 2014)
1025 (vw)	ν(COC)	(Jutier et al. 1987; Kovalenko et al. 1956)
1003 (m)	ν(COC)	(Jutier et al. 1987; Kovalenko et al. 1956)
	ν(ring)	(Watanabe, Hayashi, and Iriai 1968)
944 (vw)	δ (CH)	(Watanabe, Hayashi, and Iriai 1968; Kovalenko et al. 1956)
	ν(COC) glycosidic linkage	(Jutier et al. 1987)
917 (vw,sh)	δ (CH)	(Watanabe, Hayashi, and Iriai 1968; Kovalenko et al. 1956)
	ν(COC) glycosidic linkage	(Jutier et al. 1987)
	δ (ring)	(Berthumeyrie et al. 2014; Bussiere, Gardette, and Therias 2014)
841 (s)	ν (NO) (O-NO_2)	(Watanabe, Hayashi, and Iriai 1968; Eisenreich and Pfeil 1983; Jutier et al. 1987; Kovalenko et al. 1956; Stewart 1997; Quye et al. 2011b; Bussiere, Gardette, and Therias 2014; Berthumeyrie et al. 2014)
749 (w)	$\delta(NO_2)$	
691 (w)	$\delta(NO_2)$	

ν_a - anti-symmetric stretching; ν_s - symmetric stretching; δ -bending
vw - very weak; w - weak; m, medium; s - strong; vs - very strong; sld – shoulder

Table IV.2 Raman assignment for cellulose nitrate

CN bands (wavenumber, cm^{-1})	Assignment	Reference
2974 vs	$\nu_a CH$	(Neves et al. 2018)
2900 s	$\nu_s CH_3$	(Neves et al. 2018)
1660 - 1615	$\nu_a NO_2$	(Socrates 2004)
1655 m	$\nu_a NO_2$	(Neves et al. 2018)
1605 - 1575 s	C=N	(Socrates 2004)
1455 w	δCH	(Neves et al. 2018)
1422 w	δOH	(Neves et al. 2018)
1300 - 1270 s,p	sNO_2	(Socrates 2004)
1374 s	δCH	(Neves et al. 2018)
1208 vw	νCO	(Neves et al. 2018)
1153 sh	νCO	(Neves et al. 2018)
1125 s	νCO	(Neves et al. 2018)
1085 m	νCO	(Neves et al. 2018)
1000 w	νCO	(Socrates 2004)
870 - 840	νNO	(Socrates 2004)
853 vs	νNO (O-NO_2)	(Neves et al. 2018)
765 – 745 m	wNO_2	(Socrates 2004)
720 – 680 m	δNO_2	(Socrates 2004)
748 w	δNO_2	(Neves et al. 2018)
694 m	δNO_2	(Neves et al. 2018)
624 m	δNO_2	(Socrates 2004; Neves et al. 2018)
570 - 500 v	ρNO_2	(Socrates 2004)
561 w - br	ρNO_2	(Socrates 2004)

ν_a - anti-symmetric stretching; ν_s - symmetric stretching; δ -bending; ρ – rocking; γ – twisting; ip – in-plane; op - out-of-plane; w – wagging; vw - very weak; w - weak; m, medium; s - strong; vs - very strong; sld – shoulder

IV.2 Cellulose acetate model film

Cellulose diacetate model film (Fig. IV.2). The assignment of the main IR bands is shown in Table IV.2.

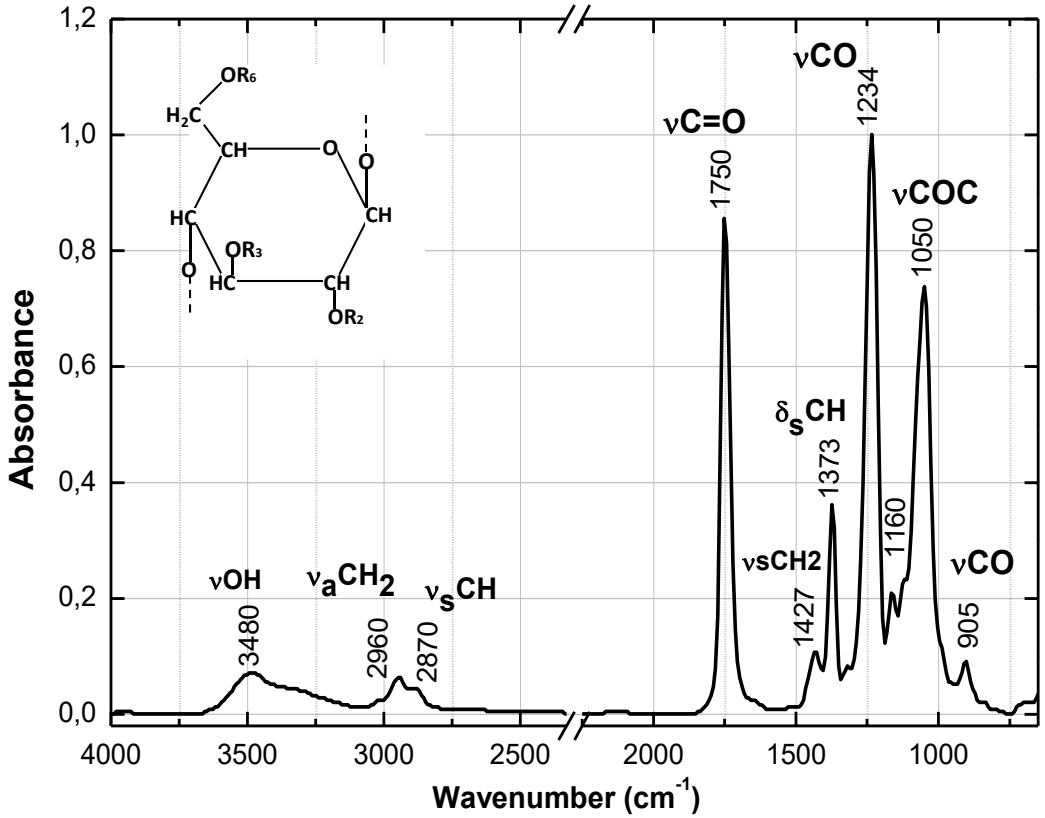


Figure IV.2 – Infrared spectrum of a cellulose diacetate model film.

Table IV.3 Infrared assignment for cellulose acetate

CA peak (wavenumber, cm^{-1})	Assignment	Reference
3430 w	νOH…O	(Shashoua 2008)
3480 w	νOH	(Zhbankov 1966; Littlejohn et al. 2013)
3000-2840 m	νCH_2 and CH_3	(Shashoua 2008; Stuart 2007)
2990	νCH_3	(Socrates 2004)
2960 w/m	$\nu_a CH_2$	(Zhbankov 1966; Sivchik, Zhbankov, and Kulakov
2870 w/m	$\nu_s CH$	1978)
1750 vs	νC=O	(Zhbankov 1966; Littlejohn et al. 2013; Ballany et al. 2001)
1743 vs	νC=O	(Stuart 2007; Shashoua 2008)
1747s	νC=O	(Babo 2006)
1463	$\delta_{as}CH_3$	(Silverstein et al. 2005)
1433m	δsCH_2 or $asCH_3$	(Babo 2006)
1430 m	δCH_2	(Zhbankov 1966; Sivchik, Zhbankov, and Kulakov 1978)
1430 m/w	δCH_3	(Socrates 2004)
1378	δsCH_3	(Silverstein et al. 2005)
1375 m/s	δsCH_3	(Socrates 2004)
1371 m/s	δsCH	(Babo 2006)
1370 m/s	δCH	(Shashoua 2008; Littlejohn et al. 2013)
1370 m/s	δCH_2	(Zhbankov 1966)
1368	δCH_3	(Stuart 2007; Shashoua 2008)
1240 s	νC=O and C-O	(Zhbankov 1966; Silverstein et al. 2005; Silva 2009)
1236 s	νC-O	(Babo 2006)
1237 s	νC=O and C-O	(Stuart 2007; Shashoua 2008)
1160 m	νCOC glycosidic linkage	(Socrates 2004; Babo 2006; Silva 2009)
1123 m	νCOC pyranose ring	(Sivchik, Zhbankov, and Kulakov 1978)
1051 s	νCOC	(Socrates 2004; Babo 2006; Silva 2009)
1027 s	νC-O	(Stuart 2007; Shashoua 2008)
950 -900 m	νC-O and ring (C5,6)	(Sivchik, Zhbankov, and Kulakov 1978)
905	νas ring or δCH	(Babo 2006)
900 w	δCH_2	(Zhbankov 1966)
840 w	νC-O	(Sivchik, Zhbankov, and Kulakov 1978)

ν_a - anti-symmetric stretching; ν_s - symmetric stretching; δ -bending; vw - very weak; w - weak; m, medium; s - strong; vs - very strong; sld – shoulder

Table IV.4 Raman assignment for cellulose acetate

CA band (wavenumber, cm^{-1})	Assignment	Reference
3040 – 2980 m -s	$\nu_a CH_3$	(Socrates 2004)
3072 m	ν_a (CH_2=CH)	(Edwards et al. 1993)
3030 - 2940 m -s	$\nu_a CH_3$	(Socrates 2004; Tsang et al. 2016)
2960 - 2860 m - s	$\nu_s CH_3$	(Socrates 2004)
1750-1740 m	νC=O	(Socrates 2004)
1739 m		(Tsang et al. 2016)
1673 w	ν(C=C)	(Edwards et al. 1993)
1604 m	ν(C=C)	(Edwards et al. 1993)
1579m w/sh	$\delta(=CH)_{ip}$	(Edwards et al. 1993)
1465 – 1415 m - w	$\delta_s CH_3$	(Socrates 2004)
1460 – 1400 m-w	δasCH_3	(Socrates 2004)
~1430 m - w	δCH_3	(Socrates 2004; Tsang et al. 2016)
1390 - 1340	δsCH_3	(Socrates 2004)
1300 m - w	ρ(CH)	(Edwards et al. 1993)
~1375 m - s	δsCH_3	(Socrates 2004; Tsang et al. 2016)
1039 m	ν(CO) terminal	(Edwards et al. 1993)
1265 – 1205 m - s	νCO-C	(Socrates 2004)
1155 m	νCOC	(Tsang et al. 2016)
1122		
1080 – 1020 w	δCH_3	(Socrates 2004)
1082		(Tsang et al. 2016)
1050 – 1040 m	CO	(Socrates 2004; Tsang et al. 2016)
1025 - 930 w	νC-O	(Socrates 2004)
1006 m	γ_w $(CH)_{op}$	(Edwards et al. 1993)
940 vw	γ_w (CH)cis	(Edwards et al. 1993)
845 – 835 m - s	νCH_3 -C	(Socrates 2004; Tsang et al. 2016)
665 – 635 w	CO	
620 – 589 m	δC=O	(Socrates 2004; Tsang et al. 2016)
450 w - br	δ(C=C-O)	

ν_a - anti-symmetric stretching; ν_s - symmetric stretching; δ -bending; ρ – rocking; γ – twisting; ip – in-plane; op - out-of-plane; w – wagging; vw - very weak; w - weak; m, medium; s - strong; vs - very strong; sld – shoulder

Appendix V

Table V.1 – Visual assessment (VA) classification. infrared peak ratios (absorptions intensities). and pH and Hardness (Shore A) measurements (averages. SD) per case study from ECC collection. Infrared spectra normalized for CH bending (1374 cm^{-1}).

VA	Samples	$\nu_a NO_2$ 1655 cm^{-1} / δCH_{1374} cm^{-1}	$s\nu NO_2$ 1282 cm-1 / δCH_{1374} cm^{-1}	$\nu O\text{-}NO_2$ 841cm^{-1} / δCH_{1374} cm^{-1}	$\nu_a NO_2$ 1655cm^{-1} / νCOC_{1160} cm^{-1}	pH	Hardness
1	ECC 981	14.0	13.2	8.3	4.8	5.3±0.1	98.8±0.5
1	ECC 1256	13.1	12.1	5.9	4.5	_____	99±0
4	ECC 6737	11.9	12.6	6.0	4.1	3.6±0.2	98.8±0.4
2	ECC 2569	11.6	12.1	5.4	4.0	5.3±0.1	98.6±0.5
1	ECC 4808	11.3	12.0	5.3	3.9	4.5±0.3	98.8±0
4	ECC 631	11.3	11.9	5.3	3.9	3.7±0.2	99±0
4	ECC 5143	11.1	9.3	4.9	3.8	4.5±0.6	99±0
1	ECC 2003	11.1	11.7	5.2	3.8	4.4±0.3	99±0
1	ECC 5433	11.0	11.1	4.8	3.7	3.9±0.2	98.8±0.4
4	ECC 8702	10.7	9.6	7.6	3.7	5.1±0.5	98.8±0.4
1	ECC 879	10.6	11.6	5.2	3.6	5.8±0.1	98.8±0.4
2	ECC 2543	10.6	10.9	5.2	3.6	5.6±0.1	98.8±0.4
2	ECC 2792	10.4	11.0	5.3	3.6	4.5±0.2	99±0
4	ECC 286	10.4	10.9	4.9	3.6	3.6±0.1	99±0
3	ECC 70	10.3	10.7	4.9	3.5	3.8±0.3	99±0
1	ECC 7774	10.3	11.0	5.0	3.5	4.1±0.3	99±0
1	ECC 1616	10.2	10.9	4.7	3.5	4.3±0.4	99±0
1	ECC 1	10.2	10.4	5.4	3.5	5.3±0.4	99±0
2	ECC 4461	10.2	10.1	4.8	3.5	5.3±0.2	98.8±0
3	ECC 22	10.2	10.6	4.7	3.5	3.6±0.2	99±0
3	ECC 6362	10.1	10.4	5.4	3.5	5.6±0.1	99±0
2	ECC 8518	9.9	10.8	4.7	3.4	5.7±0.2	98.6±0.9
2	ECC 6287	9.9	9.7	5.0	3.4	3.7±0.3	99±0
1	ECC 5142	9.9	10.5	4.9	3.4	3.4±0.1	98.8±0.4
2	ECC 2416	9.9	10.0	5.4	3.4	4.1±0.4	99±0.5
3	ECC 6083	9.8	9.7	5.1	3.4	4.7±0.2	99±0.4
5	ECC 554	9.7	10.3	4.9	3.3	3.4±0.2	99±0
2	ECC 1149	9.7	10.3	4.7	3.3	5.4±0.3	98.8±0
2	ECC 1536	9.4	9.6	4.6	3.2	5.2±0.4	99±0
2	ECC 7208	9.3	9.9	4.7	3.2	3.6±0.3	98.8±0.5
2	ECC 8708	9.1	9.8	4.7	3.1	3.8±0.1	99±0
4	ECC 5063	9.0	10.1	4.7	3.1	4.6±0.6	98.8±0
2	ECC 4466	8.9	9.1	5.2	3.1	5.6±0.2	99±0
1	ECC 5148	8.9	9.6	4.8	3.0	4.5±0.2	99±0
2	ECC 8411	8.8	8.5	3.9	3.0	4.7±0.2	98.8±0.4
3	ECC 2012	8.8	9.4	4.8	3.0	4.4±0.3	98.6±0.9
4	ECC 7959	8.8	9.4	4.4	3.0	4.3±0.2	98.4±0.4
2	ECC 2799	8.8	9.1	4.8	3.0	5.4±0.1	98.2±0.9
3	ECC 2219	8.7	9.6	4.4	3.0	4.0±0.2	98.8±0.4
3	ECC 6844	8.7	9.2	4.2	3.0	5.2±0.1	98.8±0.4
1	ECC 7364	8.7	9.0	4.6	3.0	4.9±0.1	99±0
2	ECC 7586	8.7	8.1	6.1	3.0	5.2±0.3	99±0
1	ECC 1236	8.6	8.6	4.8	3.0	5.0±0.2	99±0
3	ECC 3736	8.6	9.2	5.0	2.9	4.5±0.2	99±0
3	ECC 7643	8.6	8.7	4.0	2.9	3.7±0.2	99±0
2	ECC 2518	8.5	9.0	4.4	2.9	5.4±0.2	98.8±0.4
1	ECC 4373	8.5	9.2	4.2	2.9	5±0.4	99±0
3	ECC 2231	8.3	8.6	5.4	2.8	4.9±0.2	99±0
2	ECC 6052	8.3	7.7	5.6	2.8	3.8±0.3	99±0
4	ECC 4233	8.2	6.9	4.4	2.8	4.7±0.2	98.8±0.4
2	ECC 3866	8.1	8.2	4.5	2.8	3.3±0.2	99±0.4
2	ECC 2636	8.0	8.9	4.0	2.7	4.8±0.4	99±0

4	ECC 6730	8.0	8.3	4.1	2.7	3.8±0.1	98.6±0.9
3	ECC 4905	8.0	8.4	4.7	2.7	4.7±0.3	99±0
1	ECC 5711	7.9	7.5	5.0	2.7	4.6±0.4	99±0
2	ECC 8461	7.9	8.2	4.8	2.7	4.1±0.5	98.8±0
2	ECC 2423	7.9	7.5	3.5	2.7	4.6±0.3	99±0
3	ECC 6084	7.9	8.6	3.9	2.7	5.1±0.3	99±0.4
3	ECC 4202	7.9	8.0	5.0	2.7	5.1±0.1	99±0.4
3	ECC 2282	7.9	8.5	3.9	2.7	4.5±0.3	99±0
3	ECC 4376	7.9	8.3	4.6	2.7	5.2±0.1	99±0
4	ECC 221	7.7	7.3	5.5	2.6	3.6±0.2	99±0
2	ECC 5984	7.6	8.5	3.9	2.6	4.5±0.5	99±4
1	ECC 5499	7.6	8.3	3.8	2.6	3.8±0.2	99±0
2	ECC 2763	7.5	7.9	3.8	2.6	4.7±0.1	98.8±0.4
2	ECC 4820	7.5	8.0	4.5	2.6	4±0.6	99±0
4	ECC 5121	7.5	7.6	4.6	2.5	5±0.4	99±0.4
4	ECC 5070	7.4	6.6	3.0	2.5	4.4±0.7	99±0
1	ECC 566	7.3	6.8	5.0	2.5	3.9±0.3	99±0
3	ECC 2806	7.3	7.7	3.4	2.5	4.1±0	98.8±0.4
2	ECC 2641	7.3	6.2	4.3	2.5	5.5±0.3	98.6±0.5
2	ECC 3991	7.1	7.3	4.6	2.4	4.9±0.2	99±0
3	ECC 7319	7.1	6.7	5.4	2.4	5.6±0.1	99±0
4	ECC 354	7.1	6.6	5.3	2.4	3.5±0.1	99±0
3	ECC 30	7.1	7.0	6.4	2.4	3.4±0.1	98.8±0.4
4	ECC 6363	7.0	6.5	5.5	2.4	3.6±0.0	98.6±0.9
2	ECC 2518	6.9	6.5	4.6	2.4	5.4±0.2	98.8±0.4
4	ECC 4318	6.9	7.4	3.4	2.4	4.4±0.0	98.6±0.9
2	ECC 1233	6.7	6.2	4.9	2.3	5.4±0.1	99±0
3	ECC 2709	6.5	7.0	3.3	2.2	5.2±0.2	98.8±0.5
1	ECC 1228	6.5	6.2	4.1	2.2	5.5±0.1	99±0
3	ECC 5064	6.5	7.1	3.1	2.2	4.5±0.5	99±0
2	ECC 6059	6.4	6.9	4.8	2.2	4±0.4	99±0
2	ECC 3899	6.4	6.6	4.1	2.2	3.2±0.2	99±0
2	ECC 2413	6.4	6.9	3.1	2.2	4±0.4	98.8±0.4
2	ECC 2905	6.2	6.0	4.2	2.1	5.4±0.4	99±0
3	ECC 3643	6.2	5.7	4.6	2.1	4.5±0.2	99±0
3	ECC 2005	6.2	5.9	4.4	2.1	4.8±0.3	97.4±1.8
3	ECC 2930	6.1	5.8	5.6	2.1	5.2±0.4	99±0
4	ECC 8696	6.0	5.9	4.6	2.1	3.9±0.1	99±0
2	ECC 4807	5.9	6.0	4.2	2.0	4.3±0.6	99±0
2	ECC 2280	5.9	5.9	4.4	2.0	4.5±0.2	99±0.4
2	ECC 4316	5.9	6.0	4.4	2.0	4.7±0.2	99±0
3	ECC 4813	5.7	5.4	4.2	1.9	3.3±0.2	99±0
2	ECC 3631	5.3	5.7	4.4	1.8	4.8±0.3	99±0
2	ECC 2804	4.8	4.6	3.5	1.6	4.9±0.2	98.6±0.5
3	ECC 66	4.7	4.6	4.0	1.6	3.7±0.2	99±0
4	ECC 2931	4.1	3.7	3.8	1.4	5.4±0.2	98.8±0
4	ECC 2203	4.1	3.9	3.4	1.4	4.2±0.3	99±0

Appendix VI – Artificial ageing

'[…] *there is a wide variance in the stability of nitrate base films*.'

(Adelstein et al. 1995)

Introduction

The inevitable decomposition of cellulose nitrate-based negatives is known (Adelstein 2002; Heckman 2010). Nevertheless, the decay of negatives with CN support is not linear, but markedly complex, being reported that sometimes negatives with 50 years are in excellent state of conservation while others after 5 years are severely degraded (Adelstein 2002). Internal and external factors have been indicated as degradation causes for CN decay[129], however, due to assorted factors, a clear attribution has not been found yet.

Aiming at understanding the chemical behaviour and predict a life span for objects made with cellulose nitrate, several investigations were performed, at the beginning focusing thermal degradation (Hill and Weber 1936; Wolfrom et al. 1955; Dauerman and Tajima 1968; Jutier et al. 1987; Brill and Gongwer 1997; Rychlý et al. 2012) and overtime giving emphasis to photooxidation decay (Sirkis 1982; Derrick et al. 1993; Quye et al. 2011; Berthumeyrie et al. 2014; Bussiere et al. 2014). Until the 1950's, cellulose nitrate thermal ageing studies were conducted mainly at high temperatures and dry conditions (Hill and Weber 1936; Wolfrom et al. 1955). Based on the results obtained from those studies the instability of cellulose nitrate was emphasized. However, over time it became clear that the ageing conditions used do not reflect the behaviour of these materials under ambient or use conditions. Since the 1990's, the role of relative humidity for the decay of cellulose nitrate has been studied (Edge et al. 1990; Adelstein et al. 1992). Cellulose nitrate photooxidation ageing studies focused mostly on museum objects that are exposed to the effects of light.

In this study, a moist heat artificial ageing was performed at $80^0C \pm 0.5^0C$ and 90%±0.2% relative humidity (RH), for 168 hours. The purposes of this test were:

A) Understand the degradation behaviour of CN film-based negatives:
   i. To establish a positive correlation between naturally aged samples (selected through a survey of CN collections) and artificially aged samples of several types of commercial films with various formats, and model films;
   ii. To find differences in the behaviour of films from different manufacturers and assorted formats and establish "risk groups";

[129] See Chapter 2, section 2.5.1, pages 58 – 61.

B) To establish *in situ* and non-destructive methods for accurate identification and assessment of negatives, aiming at:
   i. Contribute to the daily practice of those responsible for film collections;
   ii. Accurate evaluation of chemical degradation and the definition of "risk groups";
C) Contribute to the definition of priorities and preservation strategies and prevent conservators and overall caretakers of prolonged exposure to solvent and acidic vapours (health hazards).

To achieve these goals, commercial films (one motion picture film, and four photographic negatives (one sheet film, three 60mm films from different brands) and a CN model film were artificially aged. The artificial ageing test was carried out for 168 hours.

FTIR studies

Based on the presence of the characteristic stretching vibrations at 1655 cm^{-1}, 1282 cm^{-1}, 841 cm^{-1} (νONO_2), the samples' film base was identified as cellulose nitrate. Except for CN reference and motion picture film, an additional peak in the carbonyl region (1740 cm^{-1}) was observed, being attributed to camphor (Stewart 1997, 86; Quye et al. 2011, 1372). Concerning the motion picture film, a shoulder, ~1760 cm^{-1} is observed (Fig. VI.1, inset, dark red).

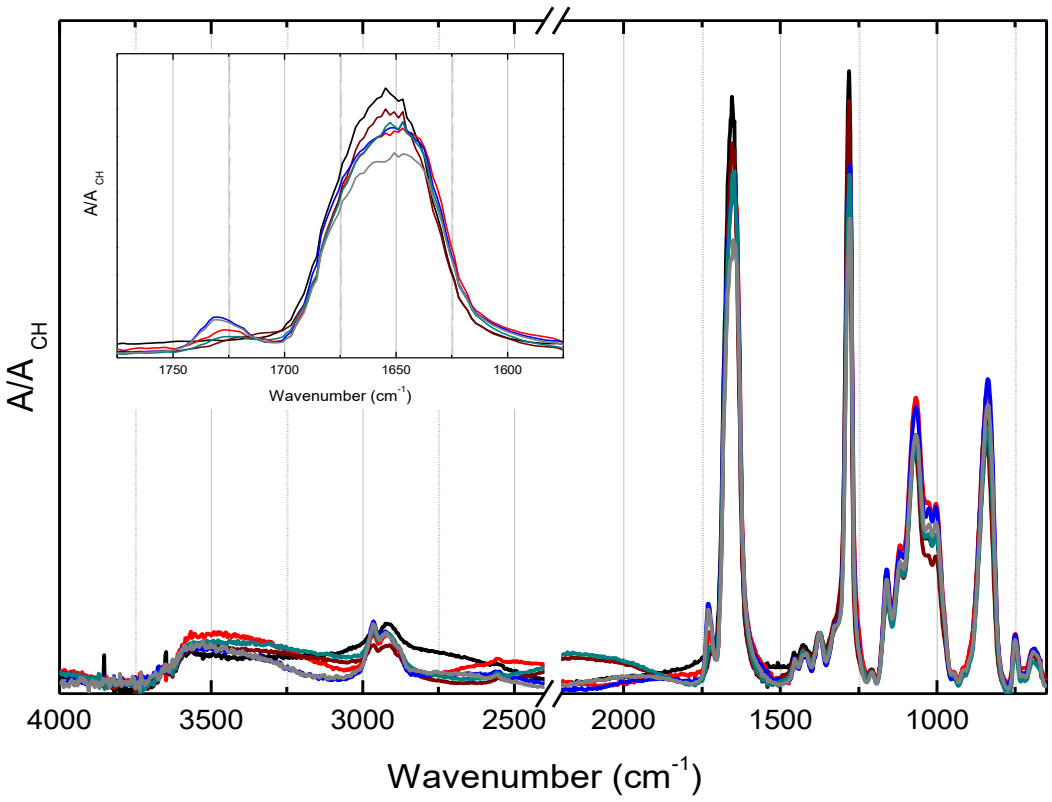


Figure VI.1 - FTIR spectra of CN reference (black), sheet film (red), motion picture film (dark red), and medium format films: A (blue), S (green) and F (grey), with absorptions normalized for CH bending (1374 cm^{-1}). Insets: detail of the C=O stretching region from 1775 to 1675 cm^{-1}.

To assess the chemical changes in the films artificially aged, a closer observation of the O-H and C=O absorptions was made, by fitting a Gaussian function. The results obtained are presented in Table VI.1.

Table VI.1 – CN samples unaged (t0) and artificially aged (t1 to t5): fitting parameters for OH, NO stretching (1655 cm^{-1}) and camphor (~1740 cm^{-1}), correlation coefficient (ρ), peak centre (μ), peak height (H), and pH ±SD. Peak normalized for δC-H at ~1374 cm^{-1}.

Sample		OH			C=O				Camphor			pH
Time[#]	ρ	H	A	μ	ρ	H	A	μ	ρ	H	A	
CN Reference												
t0	0.818	0.237	85.1	3481	0.993	8.53	435.5	1653.7				6±0.1
t1	0.943	0.871	451.2	3525	0.993	7.76	418.0	1654.9				
t2	0.887	0.617	244.6	3490	0.995	10.36	546.9	1654.4				
t3	0.966	0.82	400.2	3521	0.955	8.42	446.1	1654				
t4	0.928	1.47	232.2	3392	0.992	8.47	493.8	1652				6±0.1
t5	0.82	0.826	407.4	3427	0.994	9.58	528.1	1653				
Sheet film												
t0	0.825	0.766	329.9	3410	0.98	8.269	420.12	1652	0.96	0.69	19.07	5±0
t1	0.976	0.751	293.9	3498	0.995	9.17	469.3	1655	0.951	-0.84	-81.3	
t2	0.966	1.21	535.3	3426	0.993	7.2	372.5	1651	0.883	0.44	14.72	
t3	0.89	0.906	289.2	3407	0.966	8.07	421.7	1651	0.958	0.45	15.39	
t4	0.952	1.97	816.0	3368	0.992	4.28	250.9	1650	0.981	0.68	54.14	3.6±0
t5	0.964	2.39	958.2	3381	0.987	5.22	302.5	1648	0.956	0.82	51.36	
Motion picture film												
t0	0.686	0.1504	537.6	3354	0.995	8.8	450.6	1654				5±0
t1	0.827	0.51	127.3	3489	0.991	9.03	487.5	1652				
t2	0.979	1.14	473.3	3441	0.995	7.78	400.6	1653				
t3	0.962	1.76	755.7	3384	0.996	6.33	326.0	1651				
t4	0.947	1.93	752.7	3380	0.996	6.88	358.6	1649				3.6±0.1
t5	0.967	1.88	720.5	3387	0.991	6.01	319.3	1650				
Film A												
t0	0.905	0.556	213.2	3462	0.986	8.43	471.1	1653	0.986	1.26	32.03	4.3±0.2
t1	0.949	0.454	184.1	3496	0.993	6.51	340.1	1656	0.984	0.90	28.58	
t2	0.859	7.69	191.0	3383	0.994	7.32	362.5	1655	0.95	0.76	22.84	
t3	0.926	0.612	329.2	3539	0.992	7.77	397.6	1655	0.959	0.99	32.9	
t4	0.951	0.733	304.3	3536	0.991	10.16	520.0	1654	0.947	1.10	24.79	3.4±0.4

Sample	OH				C=O				Camphor			pH
Time[#]	ρ	H	A	μ	ρ	H	A	μ	ρ	H	A	
t5	0.917	0.954	589.2	3431	0.98	6.4	375.5	1652	0.962	1.05	31.78	
Film S												
t0	0.769	0.2091	814.3	3340	0.992	8.44	460.8	1653	0.959	0.64	27.55	4±0.1
t1	0.939	1.156	496.6	3456	0.989	8.34	487.8	1650	0.67	0.44	9.3	
t2	0.914	0.53	224.2	3510	0.995	8.17	406.3	1655	0.948	0.46	27.79	
t3	0.91	0.814	360.3	3457	0.979	6.59	388.6	1650	0.93	0.53	15.6	
t4	0.769	0.781	454.5	3452	0.996	7.67	383.47	1655.4	0.951	0.82	48.89	3.5±0.3
t5	0.91	0.87	330.7	3461	0.987	10.79	577.16	1653.4	0.97	0.75	23.45	
Film F												
t0	0.878	0.554	193.8	3468	0.987	7.47	424.7	1653	0.886	1.06	30.84	4.3±0.2
t1	0.7	0.727	158.2	3426	0.996	10.34	526.4	1655.55	0.751	0.99	38.87	
t3	0.921	0.709	402.0	3515	0.991	7.34	425.0	1654	0.972	1.04	33.36	
t4	0.905	1.07	531.5	3436	0.983	8.68	461.3	1651	0.954	1.12	25.14	3.3±0.2
t5	0.925	0.62	213.9	3454	0.975	6.59	384.9	1653	0.952	1.09	24.82	

[#]t0, t1=24h; t2 =96h; t3 =120h; t4 =144h, t5 =168h.

Except for sheet and motion picture films, a minor increase of the peak intensity was observed in the O-H stretching region. In the C=O stretching region, it was found that the decrease in the intensity of the peak is not linear during the ageing test, as an increase of its intensity followed by a decrease is observed in Table VI.1. This fact may be attributed to the formation of degradation products (aldehydes and peroxides) that are also detected in this spectral region. Concerning the plasticizer, camphor, similar behaviour was observed, initially, a decrease in the peak intensity, followed by its increase, indicating the formation of degradation products.

Raman studies

Unaged and artificially aged films were also analysed by Raman spectroscopy. Significant spectral changes were observed mostly for sheet and motion picture films, confirming the results obtained by μ-FTIR analysis. In Figures VI. 2 to VI.7, the Raman spectra of the samples CN reference, sheet film, motion picture film, and medium format films (A, S and F) (t0, t= 96h, t= 168h) are presented.

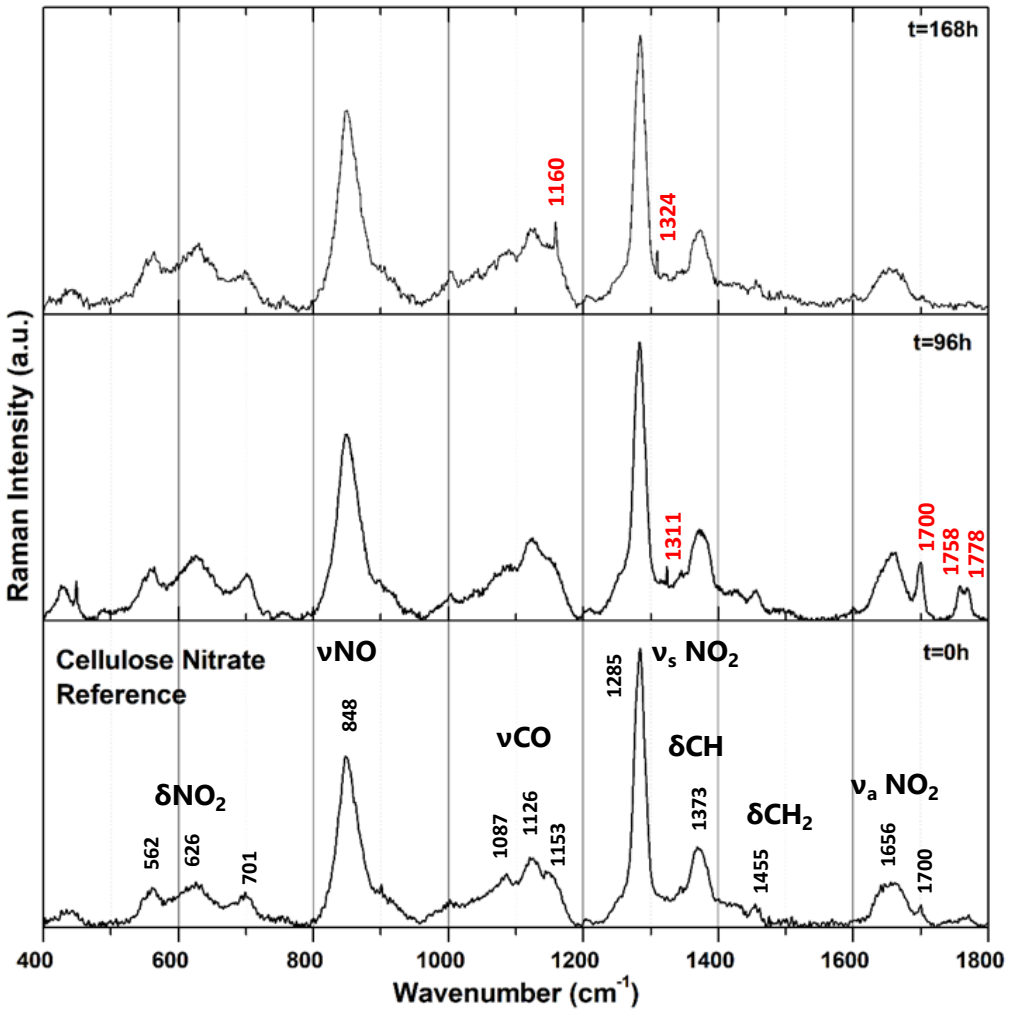


Figure VI.2 – Raman spectra of CN reference with spectral region assignments, at t=0, t=96h, and t=168h.

In Fig. VI.2 the peaks assignment for CN are presented (bottom). Additionally, a peak at 1700 cm^{-1} associated with the carbonyl function, is observed. After 96h ageing, there is an increase of the intensity of the peak at 1700 cm^{-1}. Additionally, a band (double peaks) at 1758 and 1778 cm^{-1} appears, possibly resulting from the formation of carboxylic acids (Socrates 2004). Probably related to CN decay, a weak peak at 1311cm^{-1} may indicate the formation of anhydrides. At 168h ageing, the peak attributed to anhydrides formation shifted to 1324 cm^{-1}. Moreover, the appearance of a peak at 1160 cm^{-1} may indicate the formation of aldehydes. Therefore, the Raman results allow suggesting that at 96h of artificial ageing the samples start to show signs of degradation. However, regarding pH values obtained (Table VI.1), the chemical decay confirmed by Raman analysis is not being reflected on the pH of the sample.

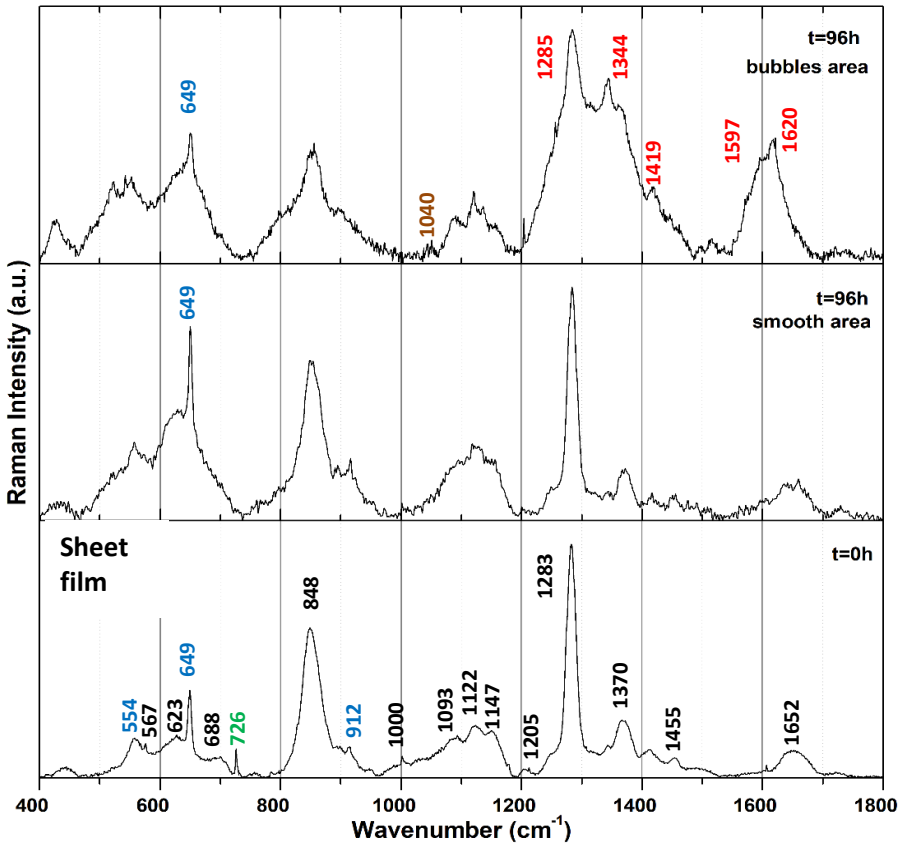


Figure VI.3– Raman spectra of the sheet film, from 400 to 1800 cm^{-1}, at t=0, t=96h, and t=168h. Wavenumbers marked in black are assigned to cellulose nitrate (CN) polymer, in blue are assigned to camphor, green to triphenyl phosphate (TPP), and in red are assigned the functional groups associated with degradation.

Concerning sheet film sample, besides the peaks attributed to cellulose nitrate, additional peaks at 554, 649 and 912 cm^{-1} (Fig. VI.3, blue) and 726 cm^{-1} (Fig. VI.3, green) were identified allowing to confirm the presence of camphor and TPP, respectively.

After 96 h ageing, extreme brittleness, amber hue and silver mirroring were observed. At this point, moving the sample was risky due to its fragility. Moreover, in the centre of the sample, a detachment, in shape of a bubble, between CN support layers was observed. It was not found a reason for this phenomenon however, it might be suggested that the concentration of degradation products formed might have caused this separation and created two layers. The two areas were analysed, showing significative differences between them. In the spectrum from the 'smooth area' (Fig. VI.3, centre) spectral changes in the region between 500 and 700 cm^{-1} (NO_2 bending vibration) and between 1000 and 1200 cm^{-1} (C-O stretching vibration) are seen, reflecting the loss of nitrate groups and TPP plasticizer. Also, a decrease of the intensity of the peaks attributed to nitrate groups (848 cm^{-1}) is noticed. As shown in Fig. VI.3 (top), comparatively, the results obtained for thinner layer detached ('bubble area') reflect the extensive decay of the film

support particularly between 1200 and 1800 cm^{-1}, where broad bands appeared indicating the formation of degradation products, e.g. carboxylic acids, and the formation of multi-nitrated rings as a consequence of ring disintegration (seen between ~1510 and 1655 cm^{-1}) (Edge et al. 1990; Socrates 2004). In addition, the appearance of a peak at ~1050 cm^{-1} suggests the development of nitric acid (Neves et al. 2018). Remarkably, despite the extensive decay of the film, peaks attributed to camphor and nitrate groups are still observed. It is not excluded the possibility that residues of gelatine from the anti-curling layer are contributing for the spectral features found, since the amino acids finger print is in the 1755 – 1700 cm^{-1} region (attributed to carboxyl groups vibration). The decrease of pH from 5 to ~4 reflects the chemical decay of sheet films (Table X.III.1).

Due to Raman technique limitations, when analysing severely degrade cellulose nitrate films, it was not possible to acquire spectra with good resolution for samples aged beyond 96h. Comparatively with FTIR analysis, Raman analysis brought new findings by being detected another plasticizer, TPP.

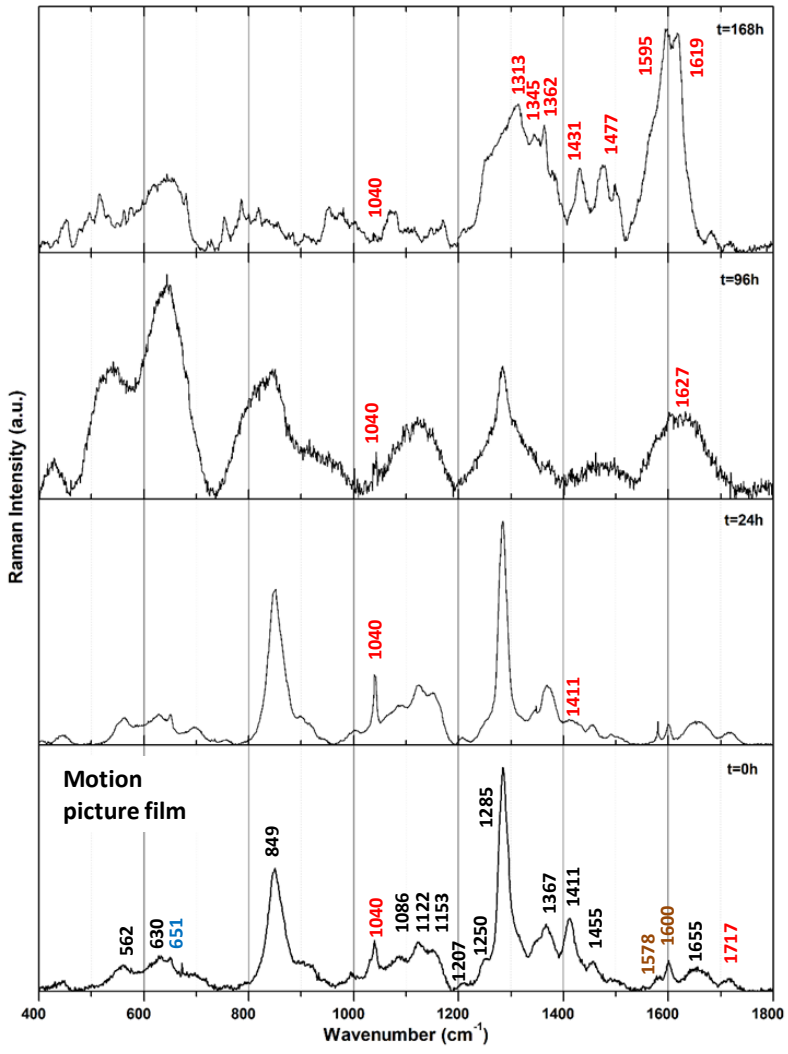


Figure VI.4– Raman spectra of the motion picture film, from 400 to 1800 cm^{-1}, at t=0, t=96h, and t=168h. Wavenumbers marked in black are assigned to cellulose nitrate (CN)

polymer, in blue are assigned to camphor, brown to phthalates, and in red is assigned to degradation.

For motion picture film, in Fig. VI.4, beside the peaks attributed to cellulose nitrate, a peak at 651 cm^{-1} (camphor, blue) and at 1578 and 1600 cm^{-1} (phthalates, brown) are seen. Again, the Raman analysis allowed to identify the presence of other plasticizers, in this case, phthalates, which was not possible by FTIR analysis. This fact may be justified by the characteristic overlapping peaks of CN that inhibit the detection of peaks attributed to phthalates. Nevertheless, the weak intensity of the peak attributed to camphor supports the findings accomplished by FTIR analysis, indicating a small concentration of this plasticizer in the film analysed.
Another peak at 1040 cm^{-1} indicates the formation of carboxylic acids (Socrates 2004), commonly correlated with CN decay (Edge et al. 1990). After 24h of ageing, an increase of the peak at 1040 cm^{-1} is observed, however, along the ageing test a decrease in the intensity of this peak occurs. After 24h a decrease of the peak at 1411 cm^{-1} (attributed to the combination of C-O stretching and C-H deformation vibrations) is observed, suggesting that the degradation has started. Besides the spectral changes found for these two peaks, no further changes were observed. These results indicate that possibly the motion picture film has different composition and moreover, degradation had started prior to the ageing test.
The analysis of the samples with ageing time 96h and 168h confirm the results of FTIR analysis and add new findings by showing significant spectral changes in the region between 1200 and 1800 cm^{-1}, reflecting denitration and evidence of further decomposition (formation of aldehydes, anhydrides and nitro compounds) that led to chain scission, similar to what was described for sheet films.
Different behaviour was observed for Films A, S and F (Fig. VI.5, 6 and 7, respectively).

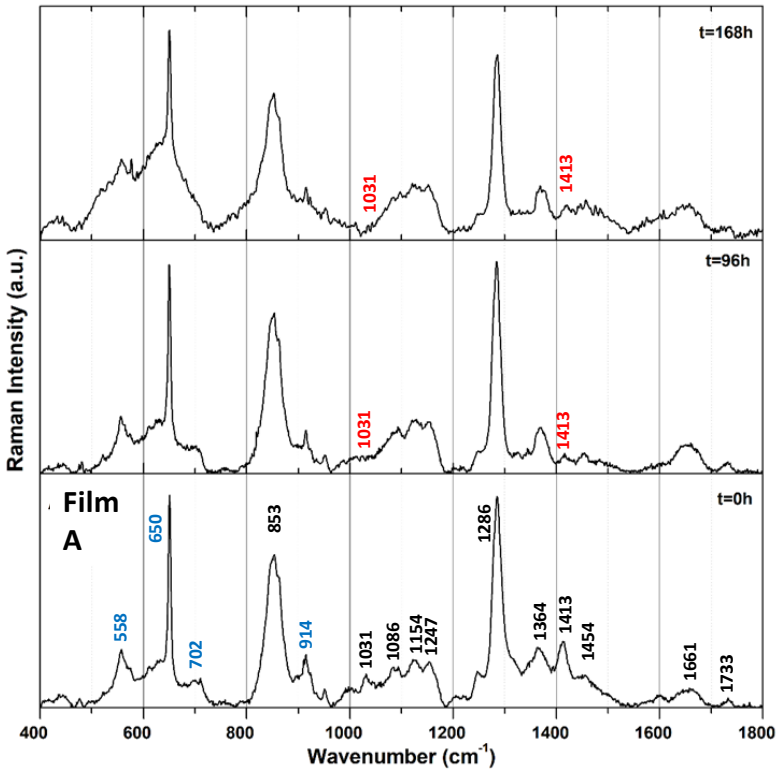


Figure VI.5– Raman spectra of the Film A (with 60 mm format), from 400 to 1800 cm^{-1}, at t=0, t=96h, and t=168h. Wavenumbers marked in black are assigned to cellulose nitrate (CN) polymer, in blue are assigned to camphor, and in red are assigned to degradation.

In Fig. VI.5 (bottom) corresponding to Film A unaged, the peaks attributed to cellulose nitrate and camphor are shown. An additional peak, at 1031 cm^{-1}, is observed. According to the literature, this peak may be attributed to a C-H stretching vibration and may not always be observed (Socrates 2004). The results obtained for the samples aged (t=96 and 168 h) shown minor spectral changes except for the peaks' decrease of intensity at 1031 and 1413 cm^{-1} and in the region between 400 and 800 cm^{-1}. Concerning these last changes, they may be related to denitration and loss of plasticizer (camphor). The decay of the film is also reflected in the pH measured, which has decreased from ~4 to 3.

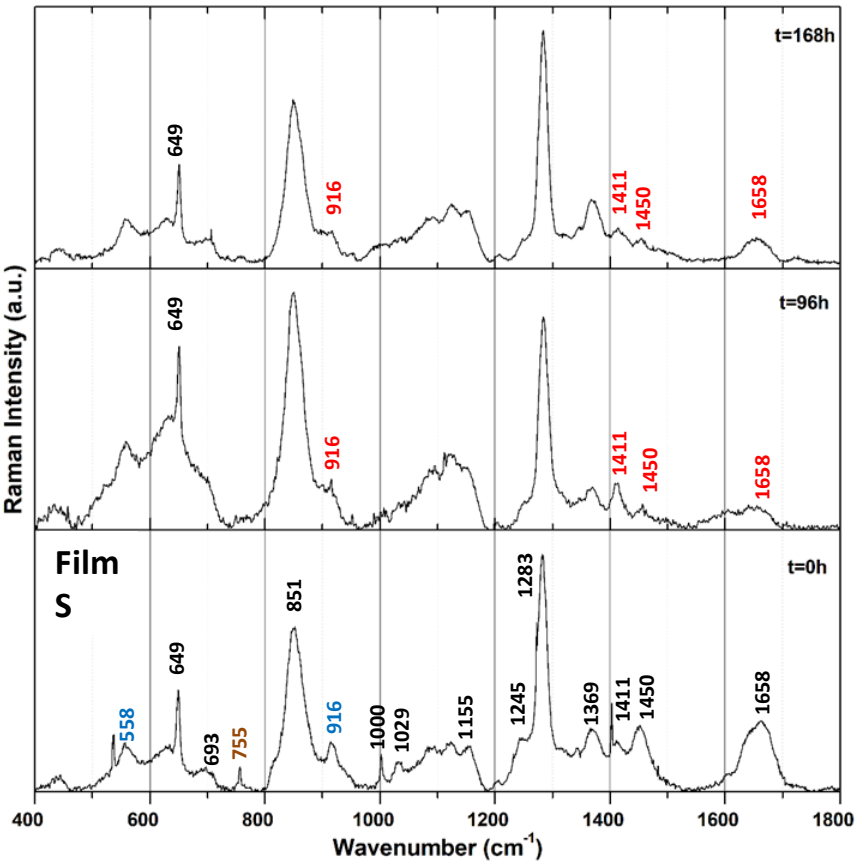


Figure VI.6– Raman spectra of the Film S (with 60 mm format), from 400 to 1800 cm^{-1}, at t=0, t=96h, and t=168h. Wavenumbers marked in black are assigned to cellulose nitrate (CN) polymer, in blue are assigned to camphor, brown to phthalates, and in red is assigned to degradation.

Concerning the analysis of Film S (Fig. VI.6), the peaks attributed to cellulose nitrate are seen, as well as peaks attributed to camphor and phthalates (plasticizers). As for Film A, minor spectral changes are observed in the course of the ageing test, besides the loss of intensity of the peaks attributed to NO bending vibration, camphor and phthalates (between 400 and 800 cm^{-1}), as well as 851 and 1283 cm^{-1} (NO stretching vibration). Again, the spectral changes seen in the spectral region between 400 and 800 cm^{-1}, might be reflecting denitration and plasticizer loss. Moreover, the increasing and broadening of the band may be attributed to the formation of degradation products (carboxylic acids). In this samples, the decrease of pH is insignificant (Table VI.1) reflecting the Fair condition of the film.

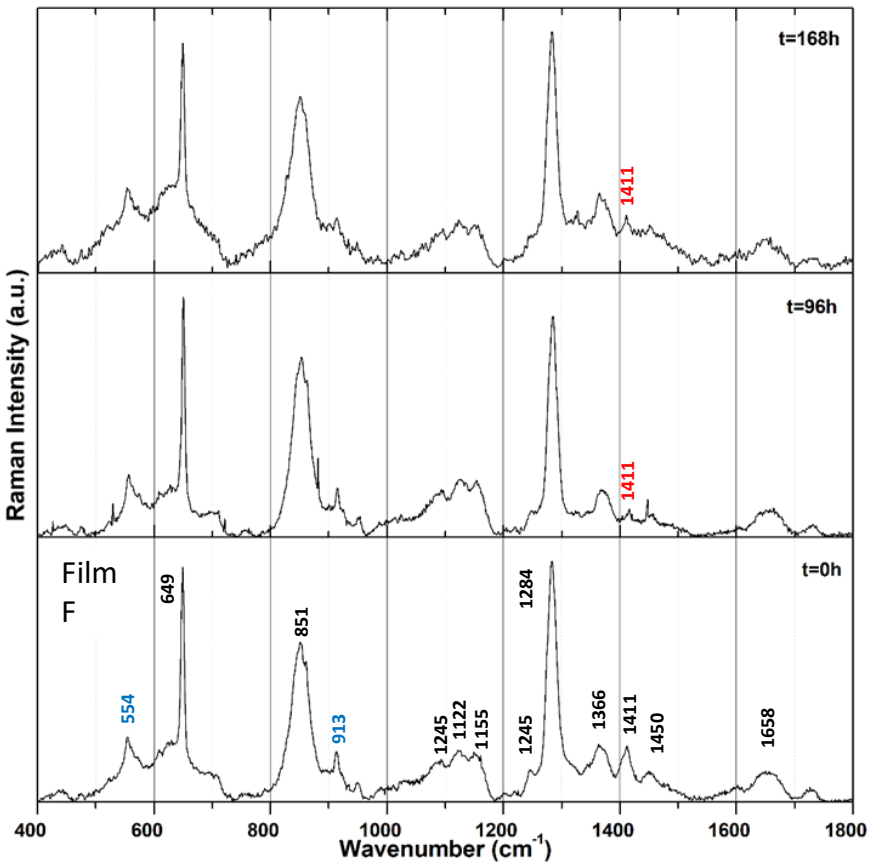


Figure VI.7– Raman spectra of the Film A (with 60 mm format), from 400 to 1800 cm^{-1}, at t=0, t=96h, and t=168h. Wavenumbers marked in black are assigned to cellulose nitrate (CN) polymer, in blue are assigned to camphor, and in red are assigned to degradation.

Similar results were obtained for Film F, for which peaks associated with cellulose nitrate and camphor were found. Regarding the spectral changes and pH, the results are identical to the previous samples from Film A and S, meaning that the film is in Fair condition.

As performed for the assessment of naturally aged films examined in this study, hardness measurements were also carried out.

Hardness

Figure VI.8 depicts the average hardness values and standard deviations obtained for all the samples analysed, according to ageing times.

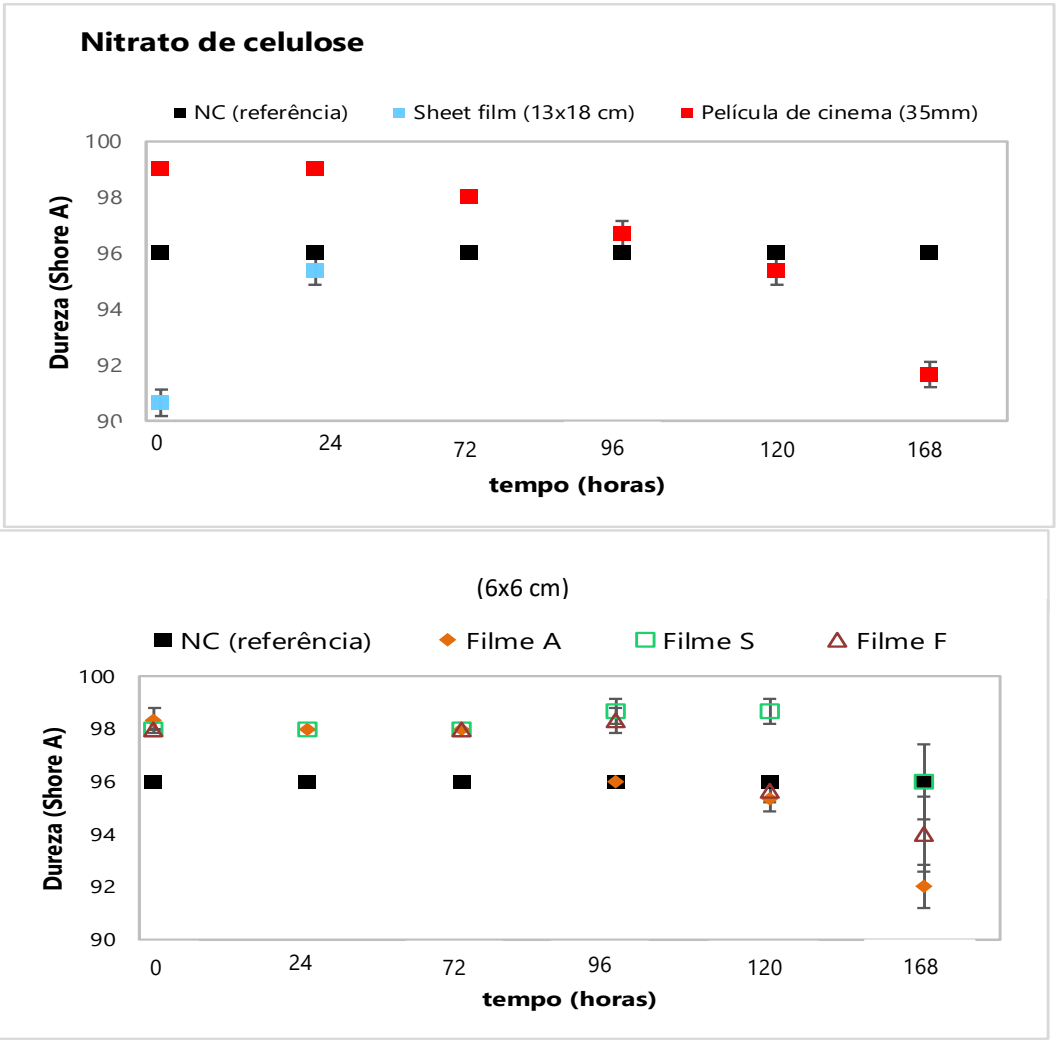


Figure VI.8 Hardness values and SD obtained for all cellulose nitrate samples artificially aged: CN model film (■), sheet film (■), motion picture film (■) (top), film A (♦), film S (□), and film F (Δ) (bottom).

No variation of the hardness was found for CN model film.
Concerning sheet film, after 24 h of ageing (t1), an increase of the hardness occurred, followed by film break. This result is consistent with the molecular condition of the CN model film samples analysed. Besides these two films (CN model and sheet films), a decrease in the hardness of the remaining films is observed, confirming the FTIR and Raman results.

Overall, motion picture film and film A have a more significant decrease in hardness. Concerning film F, a minor decrease from 98 to 96 occurs, confirming the Fair condition of the samples after ageing.

Conclusion

The findings achieved with this preliminary ageing test allowed to confirm that it is possible to assess the condition of cellulose nitrate film-based negatives by performing FTIR and Raman analysis and with pH and hardness measurements.

The Raman analysis complemented the FTIR results by identifying the plasticizers present in each type of films studied. It was also possible to confirm that during degradation, camphor is retained in the bulk of the polymer while the other plasticizers (TPP and phthalates) are completely lost. Moreover, according to FTIR and Raman analysis, comparatively, with the other pristine films, for motion picture film a lower concentration of camphor was found. Additionally, based on Raman analysis, different spectral features for samples severely degraded (sheet and motion picture films) were found. Yet in this study, I was not possible to clarify these results, which demand future work.

A positive correlation between the spectral changes and hardness measurements was obtained, showing that as denitration and chain scission evolves, hardness decreases. This finding is particularly important considering that for most the naturally aged negatives studied insignificant spectral and hardness changes were observed. As shown in this test, Raman analysis provided more information about the molecular condition of films that could be related with hardness and pH measurements. However, for naturally aged negatives, the large amount of historical films selecetd inhibited to perform this approach. Nevertheless, given the similarities between historical films and those submitted to artificial ageing, it is concluded that the artificial ageing test reflect the chemical behaviour of historical films. Therefore, according to the overall results obtained it is possible to suggest that the negatives for which hardness is in the range of 99 to 98 are in Good to Fair condition, and below that range it should be considered that ongoing degradation may lead to a fast decay of the negatives. This finding contributes for the establishment of a new methodology for assessing the preservation condition of the negatives, and, concerning preservation strategies, for the definition of priorities.

Regarding pH, the results allowed to confirm the polymer decay may be assessed by pH decrease, however, due to the presence of gelatine layers the results might not reflect the spectral changes occurring in the negative support.

This artificial ageing test also allowed concluding that the film-based negatives have different degradation behaviours according to the film type and, consequently to thickness. The results obtained suggest that sheet film and motion picture film degraded faster than roll film with medium format (Film A, S and F). The retention of the degradation products on the bulk of thicker bases and/or different films' compositions may be the origin of these diverse behaviours. Again, these results are conferring with the obtained for the naturally aged negatives studied.